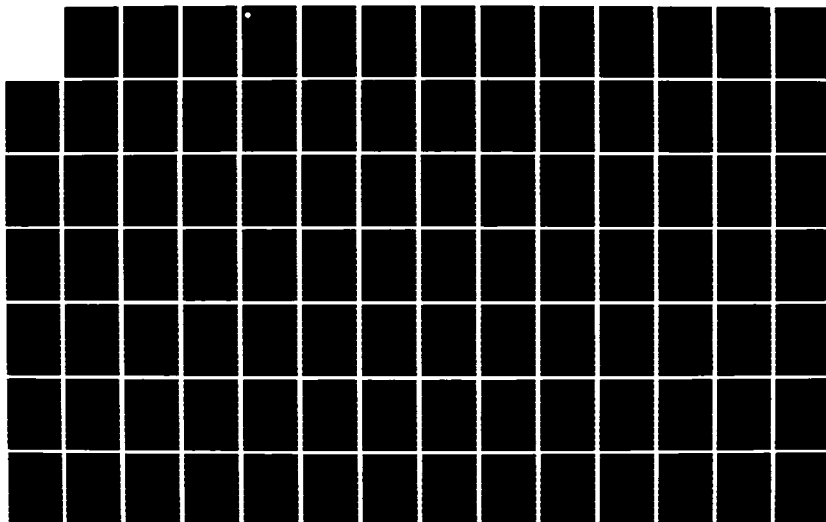THE PURIFICATION OF A DMSO-WATER (DIMETHYL SULFOXIDE)
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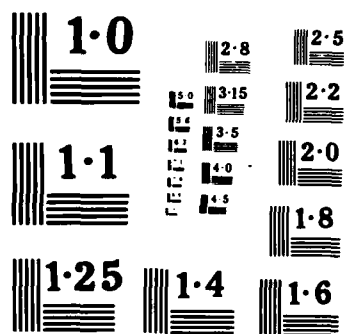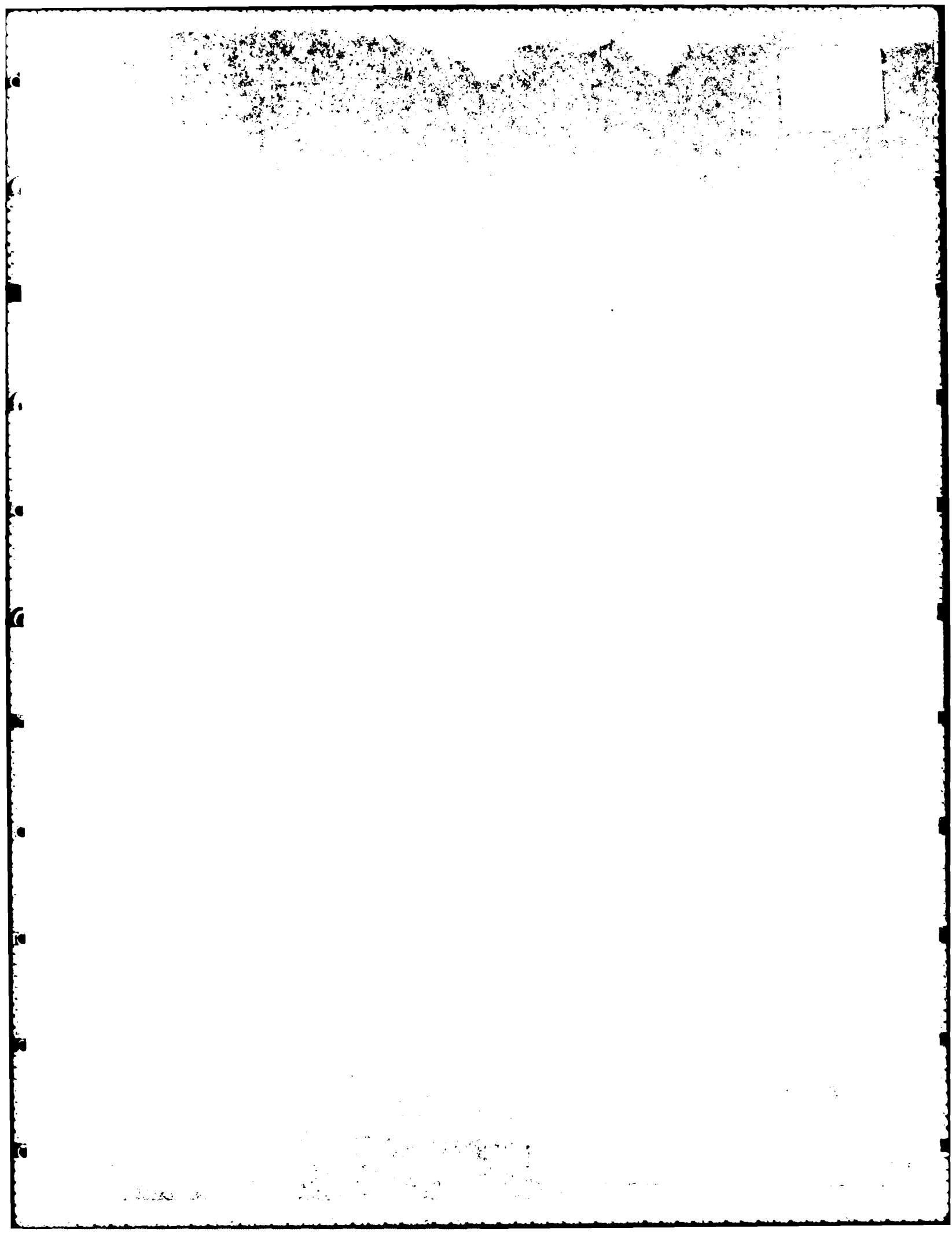TECH TERRE HAUTE IN D H BRAMER MAY 86

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THE PURIFICATION OF A DMSO-WATER SYSTEM

BY MELT CRYSTALLIZATION

A Thesis

Submitted to the Faculty

of

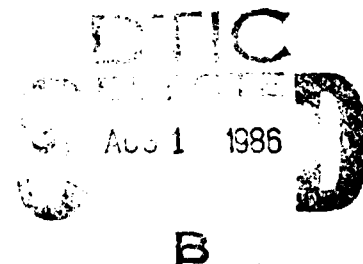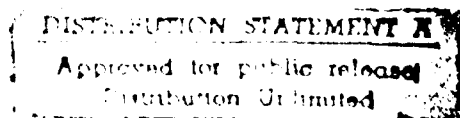Rose-Hulman Institute of Technology
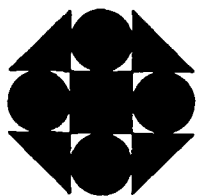Terre Haute, IN 47803

by

David H. Bramer

In Partial Fulfillment of the

Requirements for the Degree

of

Master of Science in Chemical Engineering

May 1986

ROSE-HULMAN INSTITUTE OF TECHNOLOGY

Graduate Council

APPOINTMENT OF FINAL EXAMINATION COMMITTEE

AND

FINAL EXAMINATION REPORT

Student ...... David H. Bramer .... Degree ..... Master of Science ......

Department ..... Chemical Engineering .... Date ...... April 23, 1986 ....

☒ Thesis   Title ... The Purification Of A DMSO-Water System By Melt Crystallization

☐ Non-Thesis

I. EXAMINATION COMMITTEE

It is requested that the following committee be appointed to conduct the final examination of the student named above.

Professor		Department
Warren W. Bowden	Chairman	Chemical Engineering
Noel E. Moore		Chemical Engineering
Stuart Leipziger		Chemical Engineering
Theodore K. Sakano		Chemistry

Requested by *WARREN W. BOWDEN* .... Approved by ..... *Sam C. Hite* ....

      Major Professor   Dept. Chairman

II. FINAL EXAMINATION REPORT

☒ Passed with recommendation for
    doctoral study

☐ Passed

☐ Failed

Date of Exam .... April 23, 1986 ....

Committee Signatures   *Warren W. Bowden* — Chm.

Noel E. Moore

Stuart Leipziger

Theodore Sakano
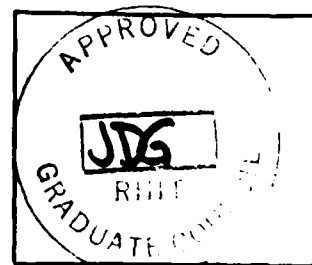
Note: When the report is complete, the Chairman of the Examining Committee should send this form
to the Director of Graduate Studies. Copies will be returned to the Chairman of the Advisory
Committee, Department Chairman, and student.

ABSTRACT

Bramer, 1Lt David, H. M.S., Rose-Hulman Institute of
Technology, May 1986. Purification of Dimethyl
Sulfoxide by Melt Crystallization. Major Professor:
Dr. Warren W. Bowden.

Melt crystallization was first used as an
industrial process in the 1950's by the Proabd
refiner.[5] A melt crystallization process consists of a
cooling step, a constant temperature period, and a
heating step. For most systems, the process can
theoretically produce a complete separation of the
components. The process can be used when other
separation processes become too expensive. The process
requires only the ability to cool and heat a system to
produce the separation.

The equipment used for this experiment was built
by Larr Etzler, a Rose-Hulman graduate student, in
1983. The heating rate was varied from trial to trial
to study its effect on the degree of separation
achieved. It was attempted to maintain a constant
cooling rate from trial to trial. The holding step
attempted to freeze as much of the system as possible.
However, the temperature limitations of the equipment
made it impossible to freeze the entire system. The
process was controlled by an AIM 65 microprocessor
using programs written in BASIC.

The main objective of the study was to produce a product of at least 99 mole percent dimethylsulfoxide (DMSO) from a DMSO-water system. The initial composition of the system was about 90 mole percent DMSO and 10 mole percent water. For every heating rate, from 2.0 $^{\circ}$C/hr to 27.8 $^{\circ}$C/hr, the composition of the product was 98.4 mole percent DMSO or greater. The mass of the product varied for different heating rates, with the faster heating rates generally producing more product.

A mathematical model was developed to represent the process by using a quasi-steady state analysis. The model could not be tested against the system because the thermal conductivity of solid DMSO was not known. Therefore, a scale-up of the process could not be completed.

A-1

ACKNOWLEDGEMENTS

I would like to acknowledge the help from the members of my committee in completing this thesis. I am especially appreciative of Dr. Warren W. Bowden for his advice throughout the problems encountered during this experimentation. Also, I would like to thank Dr. Stuart Leipziger for his guidance and time. Finally, I would like to thank Frank Cunning and Bill Lorenz for their help.

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NOMENCLATURE

A – number of moles for component A (mole)

A_0, A_1, A_2 – number of moles for component A in the feed, fraction 1, and fraction 2, respectively (mole)

B – number of moles for component B (mole)

B_0, B_1, B_2 – number of moles for component B in the feed, fraction 1, and fraction 2, respectively (mole)

C_1, C_2, C_3, C_4 – constants for mathematical model equations

ΔH – change in enthalpy (kcal)

ΔH_f – heat of fusion (kcal)

k – thermal conductivity (cal/sec m $^\circ$C)

N – thermodynamic efficiency

N_i – number of moles of component i (mole)

p – density (gm/cm^3)

r – radius (cm or in)

R – gas constant (cal/ mole $^\circ$K)

R_1 – outside radius of coil (cm or in)

R_2 – radius of crystallizer (cm or in)

R_3 – inside radius of coil (cm or in)

s – radial position of interface (cm or in)

S_1 – radial position of interface closest to coil (cm or in)

S_2 – radial position of interface closest to crystallizer wall (cm or in)

S_3 – radial position of interface inside coil (cm or in)

ΔS – change in entropy (cal/$^\circ$K)

ΔS_{fract} – change in entropy for a fractionation process (cal/$^\circ$K)

ΔS_{mix} – change in entropy for a mixing process (cal/$^\circ$K)

ΔS_{sep} – change in entropy for a separation process (cal/$^\circ$K)

ΔS_0, ΔS_1, ΔS_2 – entropy relative to pure components for the feed, fraction 1, and fraction 2, respectively (cal/$^\circ$K)

t – time (sec)

t_p – period of time between temperature changes for mathematical model (sec)

T_f – freezing temperature ($^\circ$C)

T_i – operating temperature ($^\circ$C)

T_1 – temperature of liquid ($^\circ$C)

T_o – temperature of working fluid ($^\circ$C)

T_x – temperature of system at point x ($^\circ$C) (for phase diagram section only)

W – energy requirements (kcal)

W_a – weight fraction at point a for phase diagram

$W_{min,T}$ – minimum energy requirements (kcal)

X_{AF} – mole fraction of component A in the feed

X_i – mole fraction of component i

X_1, X_2, X_3 – dimensionless positions of interface 1, 2, and 3

INTRODUCTION

Melt crystallization is primarily a batch process which utilizes the difference in the melting temperatures of two or more components to achieve a separation.[5] During the process, a system is cooled until a desired percentage is solid. The remaining liquid is drawn off and the solid is then heated at a desired rate. The liquid is drawn off in separate fractions until the desired composition is reached. As the melting progresses, the liquid will become enriched in the lower melting component. Also, the solid will become richer in the higher melting component. By repeating this process, a desired composition of either the liquid or the solid can be reached. For an experimental or industrial size refiner, the crystallizer must be designed specifically for a given system.[5] The first apparatus designed was the Proabd refiner developed in the late 1950's.[5] This refiner was used to separate naphthalene derived from coal tar from closely boiling thionaphthalene.

Objectives

The four objectives for this project with melt crystallization are as follows:

(1) To purify a dimethyl sulfoxide (DMSO) system by melt crystallization with water being the impurity.

(2) To develop a program to control both the cooling and heating process.

(3) To develop a mathematical model to represent the cooling and heating process which occurs during melt crystallization.

(4) To compare the energy requirements for the separation of the DMSO-water system used in this experiment by melt crystallization with the minimum energy requirements for the same degree of separation achieved.

The background for melt crystallization will be discussed in the literature survey. This will explain how the first objective can be accomplished. The others are derived from the results of the project and are discussed in the Results and Discussion section.

Literature Survey

Melt Crystalization

Many times crystallization has been used to
produce a very pure product with inorganics and some
organics.[2] However, this is not always the case. As
the crystals form, impurities may become trapped in the
solid. A pocket of an impurity is called an inclusion.
The inclusions can distort some of the properties of
the solid. For example, crystal growth rates are known
to increase in the presence of inclusions.[10] Irregular
growth rates can drastically reduce the efficiency of a
separation process.[10] Also, the freezing point of the
solid can be reduced when impurities are present. If
the temperature is reduced below the impurity's
freezing point, the inclusion may freeze.[10] Once the
freezing process is completed and the heating has
begun, another problem can occur. In order to obtain
the pure product, the inclusions must be removed. The
regions of higher impurity content will generally melt
first.[10] As the inclusions melt, the impurity will
attempt to flow down through the solid. If channels

or cracks are present, bulk drainage which is the flow due to gravity only may occur.[10] The problem arises in separating the liquid phase from the solid phase. Liquid drops will adhere to the solid as the impurities flow through the solid. Washing the solid with the original mixture will remove some of the impurities. However, the solid will still contain some impurity. Another problem which could occur is that pieces of solid could fall into the liquid, causing a decrease in the amount of product.

There are several advantages offered by melt crystallization. First, melt crystallization should theoretically produce a 100% pure product. Second, there are no extreme pressure requirements for the process. Third, depending on the system, the temperature requirements for the process are not too extreme. These advantages can make a melt crystallization process for certain systems very appealing. However, some improvements need to be made to the technique in separating the liquid phase from the solid to use these advantages to the fullest.

Phase Diagrams

Generally, most separation processes, including melt crystallization, utilize the tendency for a system to establish equilibrium between the different phases of a system to achieve separation of the components. Crystallization utilizes the equilibrium established between the solid and liquid phases in the mixture. By utilizing solid-liquid equilibria, crystallization processes provide the most selective of all separation methods. However, the techniques to actually separate the two components which are in contact with each other are the least developed.[9] Theoretically, a crystallization process should achieve one hundred percent separation. However, the two phases are always in contact with each other which makes complete separation nearly impossible. Solid-liquid equilibrium is similar to liquid-liquid or vapor-liquid equilibria but is more difficult to model.[9] This difficulty arises because of the composition of the solid phase. A solid does not usually have a uniform composition throughout and the composition at any one point is difficult to determine.[9]

The most accurate way to model a system of a solid and a liquid phase in equilibrium with each other is from experimental data. This data should show the thermal effects caused by the release of the latent

heat during controlled heating or cooling.[15] From this experimental data, a phase diagram for the system can be determined. A phase diagram is a basic summary of the equilibrium conditions established by the system of two or three components as a function of composition, temperature, and pressure.[15] It is applicable only when thermodynamic equilibrium has been established.[15] During melt crystallization, the system will depart from equilibrium because of the large temperature gradient across the cooling or heating interface. For a system undergoing melt crystallization, a phase diagram would predict the maximum degree of separation of the components.[15] Therefore, the results predicted by a phase diagram will be incorrect because of the departure from equilibrium during melt crystallization. To approximate equilibrium conditions during the process, the cooling or heating must be performed at a very slow rate.[15] However, the system can still depart from equilibrium depending on the stability of the equilibrium established by the components. For the results from a phase diagram to be useful, the effect of the departure from equilibrium must be considered.[15]

The following discussion concerns the simple phase diagram in Figure 1. More complex phase diagrams which consist of multiple simple phase diagrams can be explained in the same manner. The weight fractions referred to in the discussion are with respect to component B.

Initially, the mixture is completely liquid, point O, with a weight fraction of W_o. The temperature is decreased to T_f. At this point, the first crystal will begin to form. To determine the composition of the crystal, move horizontally to the solidus line at point g. At this point the weight fraction is W_g, which is greater than W_o. The mixture will continue to crystallize as the temperature continues to decrease. As the solid continues to form, it will become richer in component B and the remaining liquid richer in component A. At any point between the liquid and solid lines, the fraction of the mixture which is solid can be determined by using the lever rule. At point i, the solid will have a weight fraction of W_j and the liquid will have a weight fraction of W_h. As the temperature reaches T_m, the mixture will be completely solid and have a weight fraction of W_o. The last drop of liquid will have a weight fraction of W_l. Even though the compositions of the solid and liquid fractions are different from the initial mixture, the composition of the final mixture will be the same as the initial.
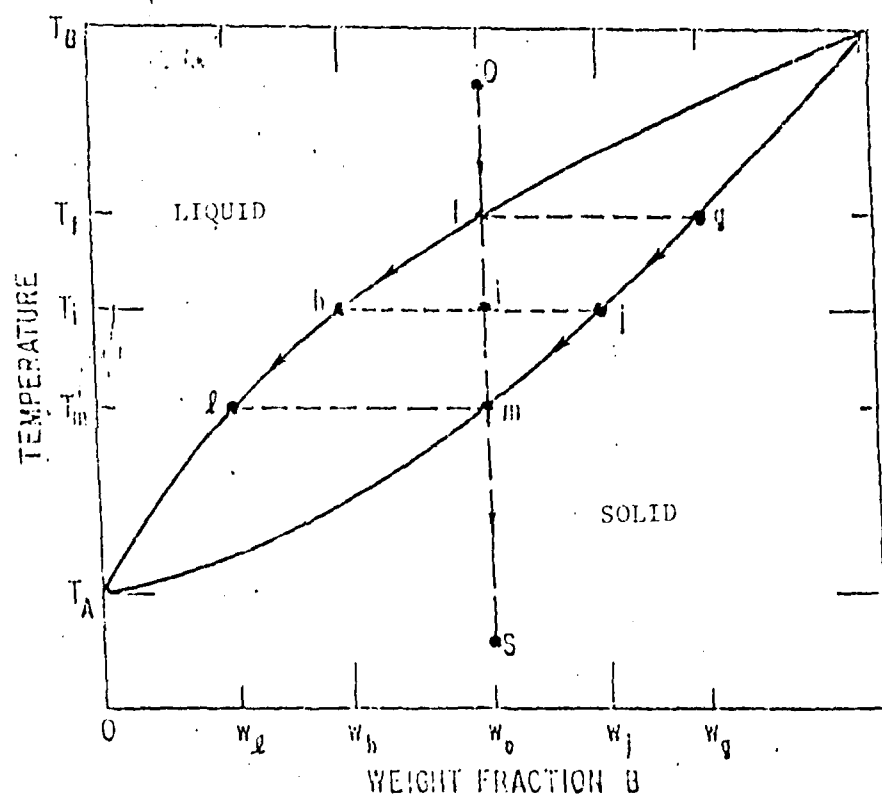
Figure 1. A simple phase diagram.[15]

A system whose phase diagram is more complicated will create problems for the separation process because the components could be more difficult to separate. An example of a of a system which has a more complex phase diagram is shown in Figure 2, the water and DMSO system. The two points of abrupt changes in the phase diagram are called eutectic points. A system which has an eutectic composition is quite common. If such a system with a composition to one side of a eutectic point is subjected to a crystallization process, the composition will remain on the same side of that point throughout the process. Another complication in this system is the formation of solid solutions. There are three different solid solutions, along with the two pure solids of DMSO and water. The formation of these solid solutions does not occur until the temperature is below $-60^{\circ}C$. If the temperature of the system is kept above this temperature, the solid solutions will not pose any difficulties in the separation process.

Equilibrium

Several properties of the equilibrium established in the system will influence a melt crystallization process. First, the shape of the equilibrium curve as the weight fraction approaches the desired product
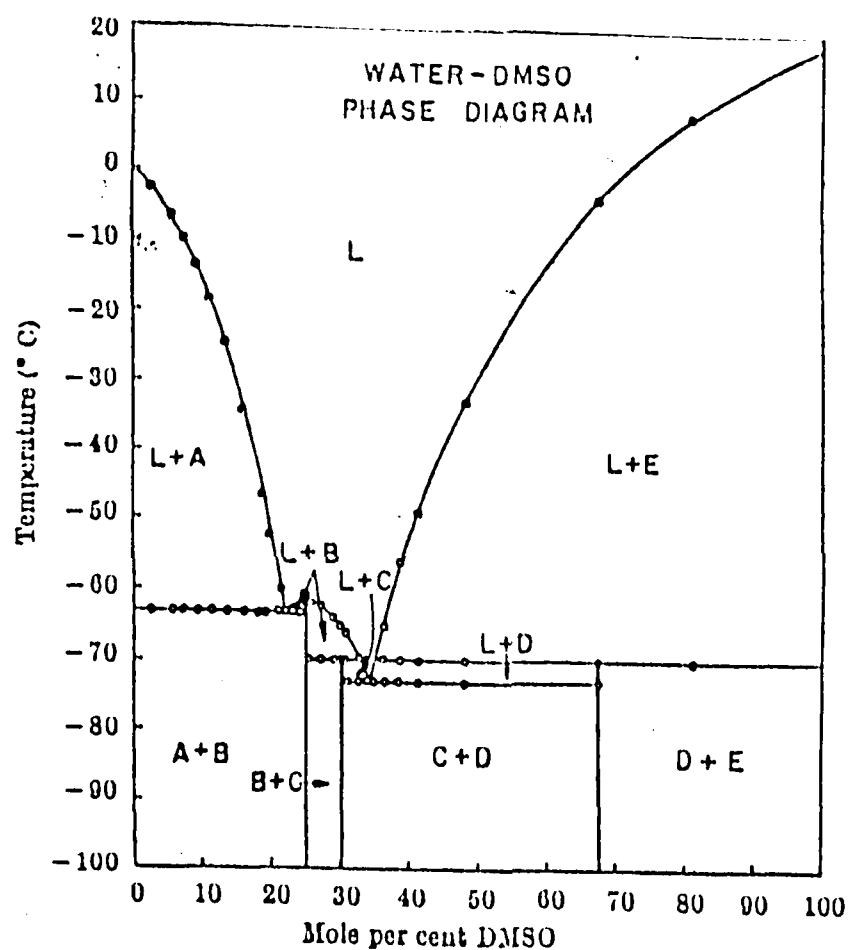
Figure 2. Phase diagram for the water-DMSO system [9]
Symbols: L, liquid; A, $H_2O_{(s)}$; B, $DMSO.3H_2O_{(s)}$; C,
$DMSO.2\frac{1}{2}H_2O_{(s)}$; D, $DMSO.\frac{1}{2}H_2O_{(s)}$; E, $DMSO_{(s)}$
$*$ -Tentative assignment

composition will have an effect. An equilibrium curve with a large slope in the proximity of the desired composition will require a large number of cooling and heating cycles to increase the concentration of the desired component. Thus, the mass of the product will be a small fraction of the initial mass of the charge. Another factor influencing the product in some systems is the presence of an eutectic. If the initial and desired compositions are on opposite sides of the eutectic, the desired process will be impossible.

Heat Transfer

Heat transfer is the most important controlling factor in a melt crystallization process. The rate of the process is determined by the rates of heat transfer and crystallization.[14] There are two primary reasons for this: (1) the latent heat must be transferred at the proper rate and (2) the appropriate temperature gradient across the freezing/melting interface must be maintained.[11] Each of these factors is equally important. The latent heat of fusion released must be removed by the working fluid to continue the freezing process. In similar fashion, the working fluid must be able to provide the latent heat required to melt the

charge. It completely surrounds the system and transports energy to and from the charge. The working fluid used for this project will be discussed in the equipment section. The rate at which the working fluid removes or adds energy is another very important factor. The effects of the cooling or heating rates on a melt crystallization process were discussed in the section on phase diagrams.

The temperature gradient across the interface is important for two reasons. It must be maintained to continue the cooling or heating process. The temperature gradient also controls the shape of the interface. For this reason, the temperature gradient should be very closely controlled. However, both long- and short-term temperature variations are virtually impossible to avoid in typical freezing or melting operations under free conduction conditions.[12] For this particular experiment, conduction is the primary type of heat transfer because the solid is stationary. The variations in the temperature can lead to changes in the degree of separation.[11] The shape of the interface can also affect the degree of separation. If there are any irregularities in the shape of the interface, impurities may become trapped at the freezing interface as it progresses.[11]

Mass Transfer

Another important factor in a melt crystallization process is the mass transfer between the solid and the liquid. The very slow diffusion of the components between the two phases establishes equilibrium in the system.[13] The reason for using slow cooling or heating rates is to attempt to approximate equilibrium conditions. As the charge solidifies, the impurities segregate at the freezing interface.[13] As more solid forms, its composition will continuously change. The composition of the liquid will also be changing. The resulting changes in composition will cause the impurity to diffuse into the liquid.[13] The diffusion is opposed by the movement of the melt to the interface caused by the solidification. The balance between the two movements will be the transfer of the impurity from the interface.[13] If the movement of the melt is greater than the diffusion of the impurity, the amount of separation of the components will be less than that predicted by a phase diagram. Therefore, the separation which occurs in a melt crystallization process depends on the mass transfer conditions.[13]

The diffusion of the impurity from the interface to the liquid will be affected by the thickness of the boundary layer. To reduce the boundary layer, mechanical stirring could be used.[13] There was no

stirring of the charge for this experiment. However, it has been proven that higher crystallization rates with some means of mixing can achieve the same degree of separation as the lower crystallization rates without mixing.[2]

Thermodynamic Efficiency

The thermodynamic efficiency of a separation process can be determined by comparing the amount of energy required with the minimum amount of energy required for the same separation. The energy requirements for the separation of two components can be determined from Equation (1).[4]

$$W = \Delta H - T_i \, \Delta S_{sep} \tag{1}$$

For an ideal solution, the change in enthalpy will be the heat of fusion plus the difference in the heat capacities of the solid and the liquid. For this system, the heat capacity difference can be considered negligible.

An entropy change for a system undergoing a process depends on the initial and final states only. The entropy change for the system undergoing separation is independent of the mechanism of separation and depends only on the amount of separation.[3]

The entropy change for a complete separation process is the opposite of a mixing process

$$- \Delta S_{sep} = \Delta S_{mix} \qquad (2)$$

For an ideal solution, the entropy of mixing is a positive quantity and is as follows

$$\Delta S_{mix} = - \Sigma N_i R \ln X_i \qquad (3)$$

where N_i is the number of moles and X_i is the mole fraction of each component and R is the molar gas constant.[3] Therefore, the change in entropy for a system undergoing a separation process with a phase change is

$$\Delta S_{sep} = \Sigma N_i R \ln X_i + \Delta H_f / T_f \qquad (4)$$

For a binary system with A moles of component A and B moles of component B, Equation (4) would be

$$\Delta S_{sep} = A R \ln A/(A+B) + B R \ln B/(A+B)$$

$$+ \Delta H_f / T_f \qquad (5)$$

If the number of moles of one component is much larger than the other, for example A>>B, then

$$\ln A/(A+B) = \ln (1-B/A) = -B/A \qquad (6)$$

and Equation (5) can be simplified.

$$\Delta S_{sep} = -B\ R + B\ R\ \ln(B/A) + \Delta H_f/T_f \qquad (7)$$

If the separation process is carried out reversibly, the change in entropy for the surroundings would be exactly equal in magnitude but opposite in sign to the change in entropy for separation. Therefore, the change in entropy represents the minimum change in entropy the surroundings must undergo to bring about the separation.[3] If the process is not carried out reversibly, the change in entropy for the surroundings would have to be greater in magnitude and opposite in sign to the change in entropy for separation. For a reversible or irreversible process, it should be a quantitative measure of the degree of separation achieved.[3]

As stated earlier, a melt crystallization process is very rarely a complete separation because the phases are always in contact with each other. This method can determine the efficiency for processes which produce only partial separations of the components.[3] The change in entropy for a partial separation or fractionation, as it is sometimes called, is

$$\Delta S_{fract} = \Delta S_0 - \Delta S_1 - \Delta S_2 \qquad (8)$$

where ΔS_0 is the entropy of the initial mixture relative to the pure components, ΔS_1 and ΔS_2 are the entropies of the two fractions.[3] Substituting Equation (7) into Equation (8), the final equation is

$$\Delta S_{fract} = R[-B_1 \ln((B_1/B_0)/(A_1/A_0))$$

$$-B_2 \ln((B_2/B_0)/(A_2/A_0))] \qquad (9)$$

Where the subscripts are for the two fractions. Equation (9) is not applicable for a system undergoing a phase change. For a separation process involving a phase change, Equation (10) can be used to determine the entropy change.

$$\Delta S_{sep} = \Delta S_{fract} - \Delta H_f/T_f \qquad (10)$$

and

$$W = R[-B_1 \ln((B_1/B_0)/(A_1/A_0))$$

$$-B_2 \ln((B_2/B_0)/(A_2/A_0))]$$

$$+ (1 - T_i/T_f) \Delta H_f \qquad (11)$$

$$\Delta S_{fract} = \Delta S_0 - \Delta S_1 - \Delta S_2 \qquad (8)$$

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$$\Delta S_{sep} = \Delta S_{fract} - \Delta H_f/T_f \qquad (10)$$

and

$$W = R[-B_1 \ln((B_1/B_0)/(A_1/A_0))$$

$$-B_2 \ln((B_2/B_0)/(A_2/A_0))]$$

$$+ (1 - T_i/T_f) \Delta H_f \qquad (11)$$

where ΔH_f is the heat of fusion and T_f is the freezing point of the pure component.

The minimum energy requirements for an isothermal separation of an ideal liquid mixture can be calculated from Equation (11)[4]

$$W_{min,T} = RT[X_{AF} \ln X_{AF} + (1-X_{AF}) \ln(1-X_{AF})] \quad (12)$$

where R is the gas constant, T is the absolute temperature, and X_{AF} is the mole fraction in the feed of component A. In the original equation in Separation Processes, the ratio of the partial pressure to the vapor pressure of both components were in the natural log terms. To arrive at Equation (12), the assumption was made that Raoult's law is applicable for this system.[4] The thermodynamic efficiency can be calculated from Equation (12).

$$N = W_{min,T} / W \quad (13)$$

The thermodynamic efficiency can be compared with the efficiencies of other processes to determine which requires less energy.

Composition Analysis

In order to determine the efficiency with the above method the compositions of the initial charge, the fractions removed from the system, and the product must be determined. There are several methods available to determine the composition of a given sample: freezing point determination, refractive index, and gas chromatography. Crown Zellerbach, a producer of DMSO, describes a gas chromatography method in a technical bulletin about DMSO.[1] This method is discussed in Appendix G. Gas chromatography was chosen because of its simplicity and reliability.

Equipment Description

Purification Equipment

The equipment used in this project was designed by Larr Etzler, a 1983 Rose-Hulman graduate student. It was modeled after the Proabd refiner, the first industrial-scale melt crystallization process. There are differences, however, so the equipment will be described in detail to make it familiar to the reader.

The mixture of DMSO and water will be referred to as the system. The container which holds the system during the process is the crystallizer in Figure 3. Also, the medium which carries energy to and from the system is called the working fluid. The working fluid is approximately 10% methanol in water solution. The reason for the mixture is that the freezing point is lower than that of pure water. The freezing point for the working fluid is $-10^{\circ}C$.

There are several constraints designed into the laboratory equipment and they will be explained. First, the working fluid flows through a closed loop and neither gains nor loses mass. In the Proabd refiner, this was not the case. The working fluid in

the industrial equipment was heated by injecting steam.
Second, since the equipment is much smaller than the
refiner, only one pump was needed. Third, the
crystallizer had no mechanical means to stir the system
during the process.

The schematic diagram in Figure 3 shows the
different parts of the equipment and the paths between
them. The most important part of the equipment is the
crystallizer. It is a glass container surrounded by a
jacket and has a copper coil on the inside. Both the
jacket and the coil are the sites of heat transfer from
the working fluid to the system. The crystallizer is
enclosed at the top by a glass dome with three
openings. Two of these openings are occupied by the
inlet and outlet of the coil which support and center
it. The third opening is used for the shaft of a
thermocouple which measures the temperature of the
system between the coil and the jacket. The coil is
made up of 3/8 inch outside diameter copper tubing
wrapped sixteen times into a 1« inch inside diameter
coil.

The crystallizer has a capacity of 1750 ml with
the coil in place. At the bottom of the crystallizer,
not shown, is a drain reservoir which holds 250 ml. A
stopcock in the drain reservoir allows samples to be
taken during the heating process.   The drain
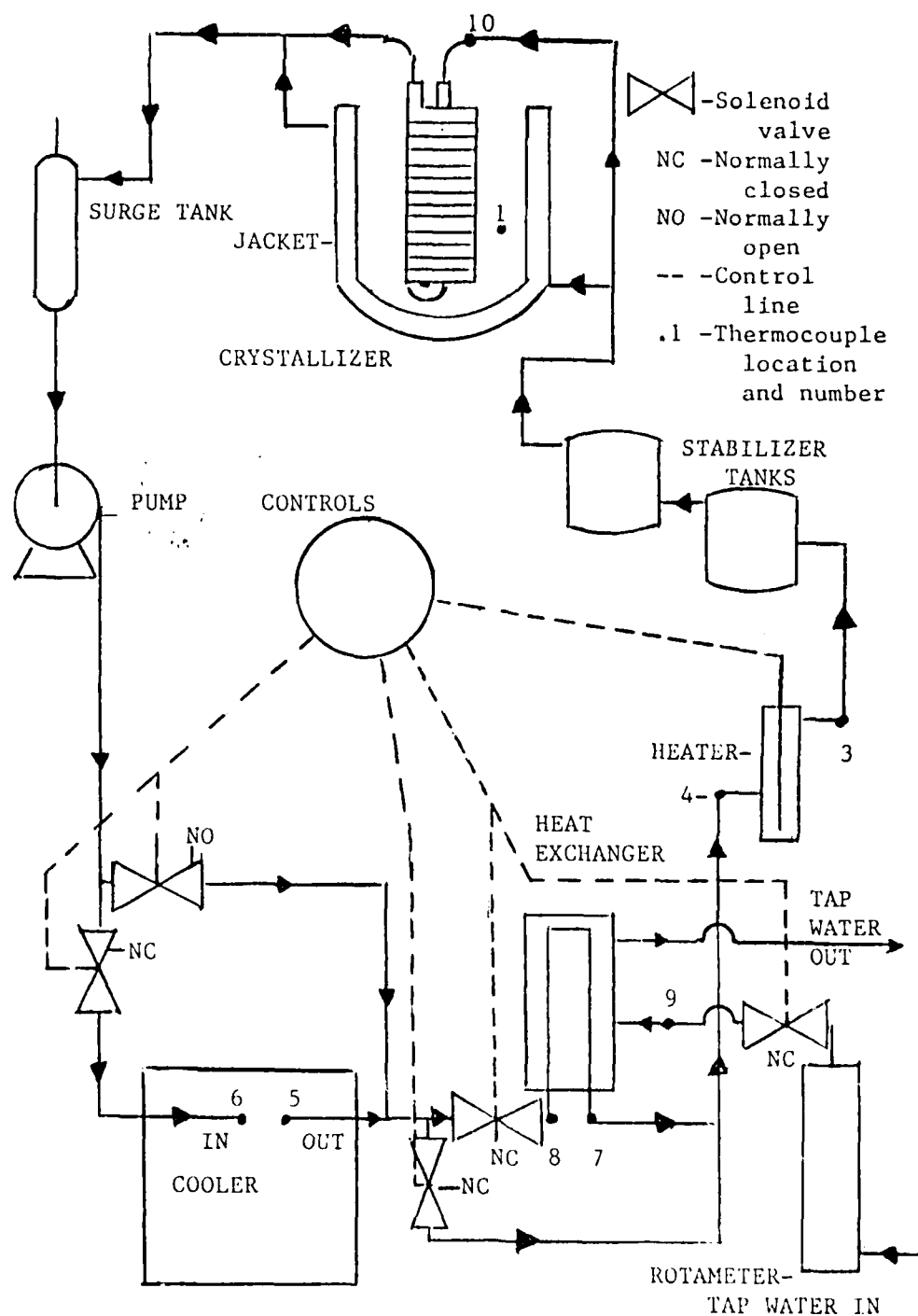
Figure 3:   Schematic diagram of the equipment used for

this experiment.

reservoir has a smaller diameter, 2 inches, than the crystallizer. A stainless steel screen separates the drain reservoir from the main chamber. This allows the liquid to drain from the solid during the heating process. The crystallizer has an inside diameter of 4 1/8 inches and an outside diameter of 5 1/8 inches. The inside wall of the crystallizer is eleven inches with the jacket beginning 2 1/2 inches below the dome support. The outside wall of the crystallizer is twelve inches. The working fluid enters the jacket at the bottom and flows out the top through ball and socket type fittings.

After the crystallizer, the working fluid flows into a surge tank. The surge tank has a capacity of one liter and is made of stainless steel. Its purpose is to keep the pump constanly supplied with the working fluid. Also, it is open to the atmosphere; which allows for expansion and contraction of the working fluid resulting from changes in temperature. The pump is a 1/12 hp centrifugal pump which can deliver a 8.7 psi head.

From the pump, the working fluid has the option of two paths to follow, depending on which solenoid valve is open. Both valves are actuated by the same signal from the microcomputer. When the signal is a low, the working fluid flows through the cooler. If the signal

is a high, then the working fluid will bypass the cooler. The cooler is a soda fountain-type cooler consisting of a compressor, fan, and an aluminum block used to transfer energy from the working fluid to the refrigerant. The cooler has a thermostat which turns the compressor off when the set temperature is reached.

There are three possible paths through which the working fluid can flow after the cooler. The working fluid can either flow through the heat exchanger, bypass it, or flow through the heat exchanger and the bypass. This can happen because the solenoid valves are actuated by different signals. The signal actuating the valve allowing flow to the heat exchanger also actuates the tap water valve. Either the heat exchanger or the heat exchanger bypass valve should always be open to allow a clear path for flow.

The heat exchanger can be used to heat or cool the working fluid depending on the temperature of the tap water. The tap water has the possibility of being entirely hot or cold, or a mixture of both. This is accomplished with tubing from each tap connected by a tee junction to the line leading to the rotameter. The heat exchanger is able to provide enough energy to the working fluid to either produce a slow cooling or heating rate when working against the cooler and the

heater. The temperature of the tap water should be around 13°C to accomplish the slow cooling or heating for this equipment. Also, the heat exchanger is able to dampen the temperature oscillations when the cooler turns on or off.

The next supplier of energy to the working fluid is the heater, a one kilowatt immersion element. The shell is a plain carbon steel tube, 11« inches long with a two inch outside diameter. A light near the manual switch indicates if the heater is on. With such a small container, the heater has the ability to create a large temperature shock to the working fluid. For this reason, two tanks were placed after the heater to mix the working fluid before it entrers the crystallizer jacket and coil. Two tanks were used to increase the mixing.

Control Apparatus

During a melt crystallization process, the cooling or heating must be controlled to achieve the desired separation. In this project, an AIM 65 microprocessor with 4K RAM was used to control the solenoid valves and heater. The microprocessor can be programmed through its assembler with BASIC or FORTH languages. BASIC was used for this experiment. The I/O (input/output)

ports on the AIM 65 can be specified to be input or output ports. This is accomplished by placing a number in a specific memory location. The memory location specifies if it is input or output and the numbers determine which port is active. A number placed in another specific memory location can specify if the port is to send or receive a signal. The output signal is five volts DC.

The five output signals from the microcomputer can activate three solenoid valves, a heater, and an alarm. The three valves are controlled by solid state relays. The valves and the heater are connected by an electronic circuit to the microcomputer. A switch in the circuit allows for the microcomputer to be disconnected from the equipment. The relays receive a signal from the microcomputer and turn on the power to actuate the valves. There are also manual switches in parallel with the relays. This allows for a valve or the heater to be turned on by either the microprocessor or the manual switch. However, if the microprocessor is connected to the equipment, both must be off to deactivate the valve or the heater.

There are manual switches for the pump, cooler, and the temperature display unit on the control board. Also, there are manual hot and cold valves for the tap water and a valve to bypass the crystallizer jacket. In this project, this valve always remained open.

The thermocouples used were 0.015 inch copper-
constantan wire. There were ten thermocouples
altogether and they were connected to an A/D converter.
The A/D (analog/digital) converter accepts an analog
signal and translates it into a digital signal. This
allows the thermocouple to communicate with the
microcomputer. Each thermocouple has its own channel
in the A/D converter. Thus, the microprocessor can
specify a channel number and the signal for the
thermocouple with that channel number can be read.
Each channel has two calibration potentiometers, one
for the zero and the other for the gain. The
thermocouples are also connected to a ten-position
selector switch. The temperature displayed depends on
the position of the display. The thermocouple numbers
in Figure 3 are determined from this.

Procedure

In this section, the procedure used to purify the system by melt crystallization will be explained. The process consisted of a cooling step, a holding time to freeze as much of the system as possible, and a heating step. The procedure for each experiment was essentially the same except for the last trial. In that particular trial, the cooling was not controlled in order to determine its effect on the product.

The DMSO was obtained from SCM in Brunswick, Georgia. It was 99^+% DMSO and the only impurity was assumed to be water. This assumption was strengthened after analysis with gas chromatography detected only one impurity. The main objective of this project was to produce industrial grade DMSO; so no further purification of the initial DMSO was performed.

The system was 10% molar water and 90% molar dimethyl sulfoxide. The amount put in the crystallizer was recorded and the crystallizer was sealed with a glass dome. The tap water flow rate was set at the 20% mark on the rotameter, about 120 ml/sec. In the first few trials, the temperature of the tap water was initially around $20^\circ C$ and decreased as the cooling

progressed. However, the time required for such a slow cooling process was unfavorable. Therefore, the tap water temperature was adjusted to around 13°C and remained constant throughout the cooling process. At this temperature, the heat exchanger along with the heater could work against the cooler to produce a slow cooling rate.

Once the system was in the crystallizer, the power for the equipment was turned on. Then the manual switches for the pump and the cooler were turned on. At some time earlier, the program FREEZ was loaded into the memory of the AIM 65. The user must type run into the AIM 65 keyboard to start the controlled cooling process. The only information required by the microcomputer to begin the cooling process is the current time in hours, minutes, and seconds. The final temperature of the cooling process remained constant throughout the project; so this was written into the program.

As the cooling begins, crystals will form on the walls inside the crysallizer. The crystals continue to grow until the most of the system is solid. The freezing point of the system was approximately 12°C. The temperature of the system was then reduced to 5°C and held there for one hour. Once the hour had passed, the stopcock was opened and the remaining liquid

drained off. The volume of the liquid was usually about 550 ml or about 34% of the initial charge. The stopcock remained open until the draining liquid flow rate was a very slow drip.

At this time, the program MELT1 was loaded into the microcomputer. This program required more information than FREEZ for the process to begin. The number of heating segments, the final temperature, and the gradient for heating the system along with the time must be typed into the microcomputer. The number of heating segments was always one for this experiment. As the heating begins, the tap water temperature was adjusted to help the heater produce the desired gradient. For low gradients, the tap water temperature was not adjusted since the heater could produce the desired results. A sample was taken at every degree increase to enable a comparson of the composition of the samples for different gradients. A sample consisted of all the liquid in the drain reservoir. The heating was continued until the temperature inside the crystallizer was about 19°C. This temperature was chosen because of the usual collapse of the solid at this temperature. Also, the melting point of pure DMSO is 18.55°C, so it is probable that no further separation would take place above this temperature.

The samples were taken in bottles cleaned and weighed before every trial. A bottle never weighed exactly the same from trial to trial, thus the reason for the repeated weighings. Once the samples were taken, they were analyzed with a Gow-Mac gas chromatograph equipped with a thermal conductivity detector. The output from the GC was sent to a Keithley data acquisition system, model 500. The data acquisition system converted the signals from the detector into a form that could be interpreted by an IBM personal computer. Software developed by Keithley and a program written by Bill Lorenz, a Rose-Hulman graduate student, took the output and determined the area percent detected for each component in a sample. This provided the results much quicker than those from a strip chart without sacrificing accuracy. Once the samples were analyzed, they were returned to the original container, a gallon bottle, to be reused in the next trial.

MATHEMATICAL MODEL

For the results from this experimental apparatus
to be useful, a mathematical model of the process is
needed. Since the cooling and heating processes were
slowly, the interface between the liquid and the solid
also moved very slow. For this reason, a quasi-steady
state analysis can be used to represent the process.
In this analysis, the system is considered to be at
steady state at any instant. After each instant, the
variables change to a new value and once again the
system is at steady state. The temperature profile
during the process is assumed to be fixed at any
instant. During the cooling process, the liquid is
cooled to its freezing point. At this time, a layer of
crystals will form on the glass wall and the coil
inside the crystallizer. This layer will continue to
grow as the freezing progresses until the two
interfaces meet. Between the coil and the center of
the crystallizer, a similar process will occur. After
a layer of crystals has formed inside the coil, the
crystals will grow until the inside of the coil is
completely solid.

The following development will be concerned with
the area between the coil and the glass wall of the
crystallizer. The derivation will be done in

cylindrical coordinates. The temperature profile wiil be in the form

$$T = C_1 \ln r + C_2 \qquad (14)$$

where T is the temperature inside the crystallizer, r is the radial position, and C_1 and C_2 are constants. It is assumed since the glass wall is thin that the temperature at the glass wall will be the same as the temperature of the working fluid at that time. The temperature of the interface between the solid and liquid is assumed to be the temperature of the liquid inside the crystallizer. Therefore, the boundary conditions at the outermost interface are as follows:

$$\text{at } r = R_2 \quad T = T_0$$
$$\text{and at } r = S_2 \quad T = T_1 \qquad (15)$$

where R_2 is the radius of the crystallizer, S_2 is the radial position of the interface, T_0 is the temperature of the working fluid, and T_1 is the temperature of the liquid in the crystallizer. For the interface at the coil, the temperature of the crystals is assumed to be the temperature of the working fluid. Also, the temperature of the interface will be the temperature of the liquid. The boundary conditions for this interface are

$$\text{at } r = R_1 \quad T = T_o$$
$$\text{and at } r = S_1 \quad T = T_1 \quad\quad (16)$$

where R_1 is the radius of the coil, and S_1 is the radial position of the interface. By substituting the boundary conditions into Equation (14) for each condition, Equation (14) becomes

$$T_o = C_1 \ln R_2 + C_2 \quad\quad (17)$$
$$T_1 = C_1 \ln S_2 + C_2 \qu\quad (18)$$
$$T_o = C_3 \ln R_1 + C_4 \qu\quad (19)$$
$$T_1 = C_3 \ln S_1 + C_4 \qu\quad (20)$$

Solving for C_1 and C_3,.

$$C_1 = (T_1 - T_o)/\ln(S_2/R_2) \qu\quad (21)$$
$$C_3 = (T_1 - T_o)/\ln(S_1/R_1) \qu\quad (22)$$

At the solid-liquid interface

$$k \, (dT/dr)_{interface} = p \, \Delta H_f \, (ds/dt) \qu\quad (23)$$

where k is the thermal conductivity of the solid, p is the density of the solid, ΔH_f is the heat of fusion per unit mass, s is the position of the interface, and t is the time. By finding dT/dr at either interface,

the change in the position of the interface with
respect to time can be determined.   From Equations
(14), (21), and (22)

$$(dT/dr)S_2 = (T_1 - T_o)/(S_2 \ln(S_2/R_2)) \quad (24)$$
$$(dT/dr)S_1 = (T_1 - T_o)/(S_1 \ln(S_1/R_1)) \quad (25)$$

Substituting Equations (24) and (25) into Equation
(23), dS_2/dt and dS_1/dt are

$$dS_2/dt = k(T_1 - T_o)/(p \Delta H_f S_2 \ln(S_2/R_2)) \quad (26)$$
$$dS_1/dt = k(T_1 - T_o)/(p \Delta H_f S_1 \ln(S_1/R_1)) \quad (27)$$

Rearranging Equations (26) and (27) gives

$$S_2 \ln(S_2/R_2)dS_2 = (k/p \Delta H_f)(T_1 - T_o)dt \quad (28)$$
$$S_1 \ln(S_1/R_1)dS_1 = (k/p \Delta H_f)(T_1 - T_o)dt \quad (29)$$

By letting X_2 equal S_2/R_2 and X_1 equal S_1/R_1 and
finding dX_2 and dX_1 which are dS_2/R_2 and dS_1/R_1,
respectively, some dimensionless groups can be
introduced. By substituting these simplifications into
Equations (28) and (29) and rearranging, they become

$$X_2 \ln X_2 dX_2 = (k/p \Delta H_f R_2^2)(T_1 - T_o)dt \quad (30)$$
$$X_1 \ln X_1 dX_1 = (k/p \Delta H_f R_1^2)(T_1 - T_o)dt \quad (31)$$

To determine the time when the interfaces meet, Equations (30) and (31) must be integrated with the limits of integration being 1 to S_2/R_2 and 1 to S_1/R_1 for X_2 and X_1, respectively, and 0 to t_p for time, where t_p is the period of time between changes in T_o. This process is repeated until $S_2 = S_1$. The total time required for the interfaces to meet can be determined by adding the t_p's together.

For the region between the inside of the coil and the center of the crystallizer, the temperature profile will be in the form of Equation (14). The boundary conditions will be as follows:

$$\text{at } r = R_3 \quad T = T_o \tag{32}$$
$$\text{and at } r = S_3 \quad T = T_1 \tag{33}$$

where R_3 is the inside radius of the coil and S_3 is the radial position of the interface. By following the same steps as in the development of Equations (30) and (31), an equation for this region can be developed.

$$X_3 \ln X_3 \, dX_3 = (k/p \, \Delta H_f \, R_3^2)(T_1 - T_o)dt \tag{34}$$

where X_3 equals S_3/R_3. By using the limits of integration for X_3 of 1 to 0, the amount of time required for this region to become solid can be

determined. By inspection of the actual process, the time required for this region to become solid is much less than the time required for the interfaces of the other region to meet. To solve the system of equations the thermal conductivity for solid DMSO is required. Unfortunately, it was not known and so the equations could not be solved. However, for chemical systems with a known thermal conductivity, density, and heat of fusion the equations can be useful in modeling the system.

RESULTS

The results for each objective will be discussed in this section.

(1) To purify a dimethyl sulfoxide (DMSO)-rich solution by melt crystallization with water being the impurity.

A melt crystallization process consists of a cooling step and a heating step. For this experiment, the heating rate was changed from trial to trial. It was attempted to maintain the same cooling rate for every trial. This was not always possible because of changing room conditions for each trial. The time required to freeze the system increased when the room temperature was higher. However, the composition of the liquid drained off after cooling was very similar for each trial. As the trials progressed, it became apparent that the cooling step was more important to the separation process for this system than the heating step. The slow cooling of the system produced a liquid which had a composition of about twice as much water as the original mixture.

The purification of the DMSO-rich solution was accomplished with every heating rate used for this experiment. For heating rates below 7.5°C/hr, the final composition was greater than or equal to 99 mole percent DMSO. Figures 4 through 10 graphically show the increasing DMSO composition of the sample with the increasing temperature of the system for these heating rates. The heating rate which produced the highest DMSO composition in the product was 5.3 °C/hr. The composition of the product for this heating rate was 99.7 mole percent DMSO. Two other heating rates, 6.0 and 7.5 °C/hr, produced compositions of 99.6 mole percent DMSO.

For the heating rates higher than 7.5°C/hr, the final composition was between 98.8 and 98.4 mole percent DMSO. Figures 11 through 15 are the graphical results for these heating rates. The differences in the product compositions for different heating rates could arise from the deviation from equilibrium is greater for the faster heating rates. Thus, the larger deviations from equilbrium produce a decrease in the degree of separation achieved which is to be expected.

Even though a difference exists between the composition for the two groups of heating rates, it is very small. This would suggest that the DMSO-water system is well suited for separation by melt crystallization. The numerical results for all heating rates are in Appendix A.
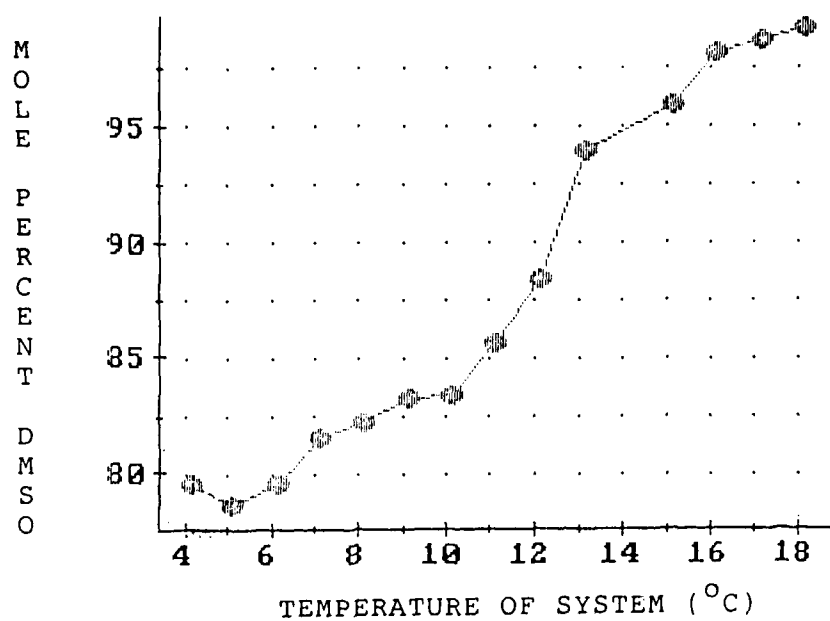
Figure 4:   Change in DMSO composition for a
heating rate of 2.0°C/hr.
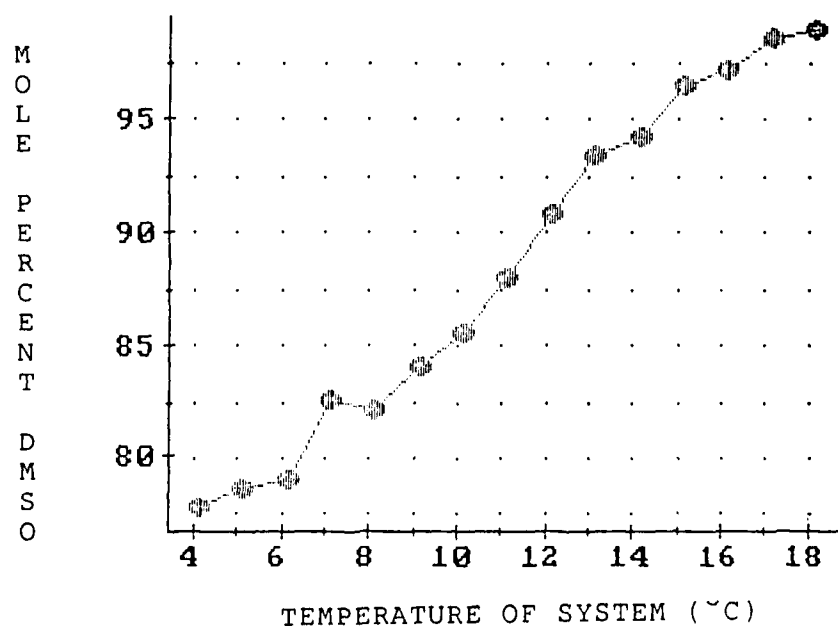
Figure 5:   Change in DMSO composition for a
heating rate of 3.0°C/hr.
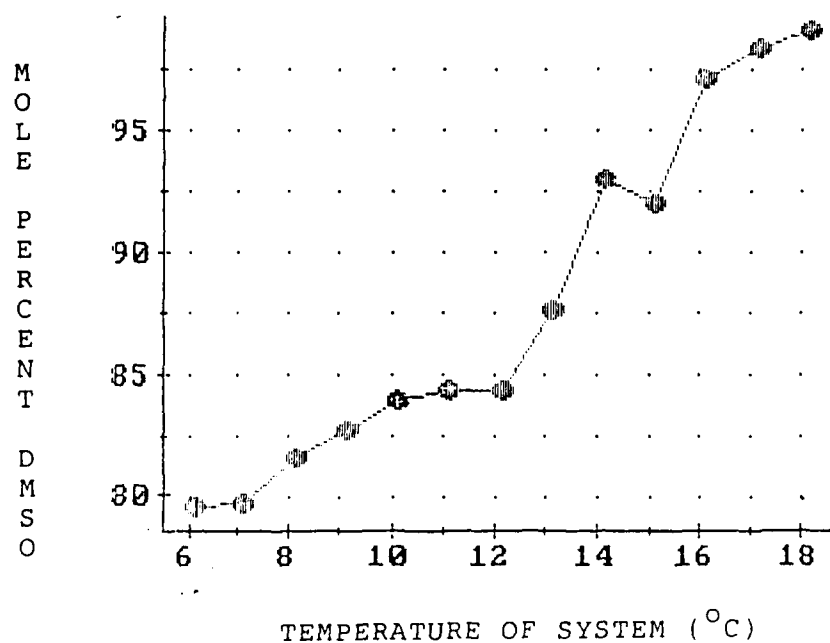
Figure 6:   Change in DMSO composition for a
heating rate of 4.5°C/hr.
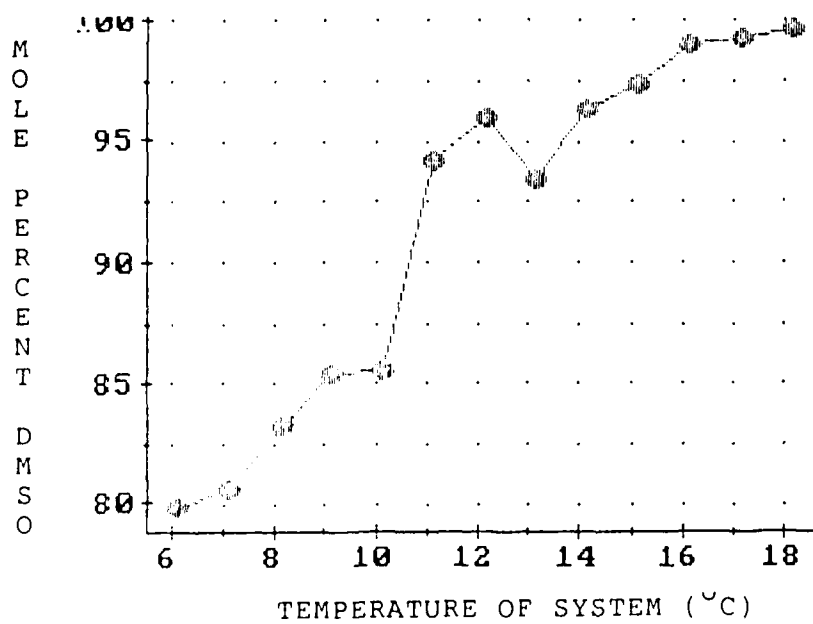
Figure 7:   Change in DMSO composition for a
heating rate of 5.3°C/hr.
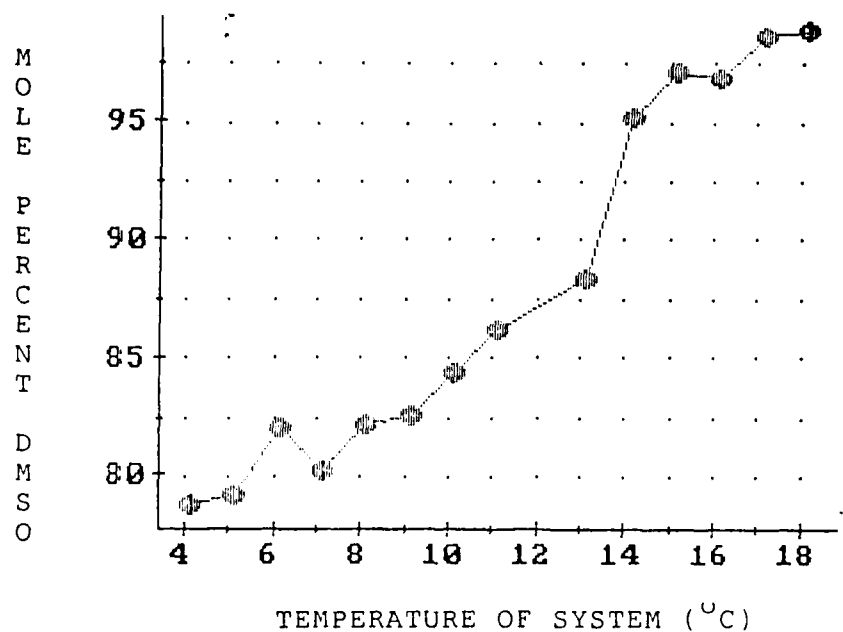
Figure 8: Change in DMSO composition for a
           heating rate of 5.4°C/hr.
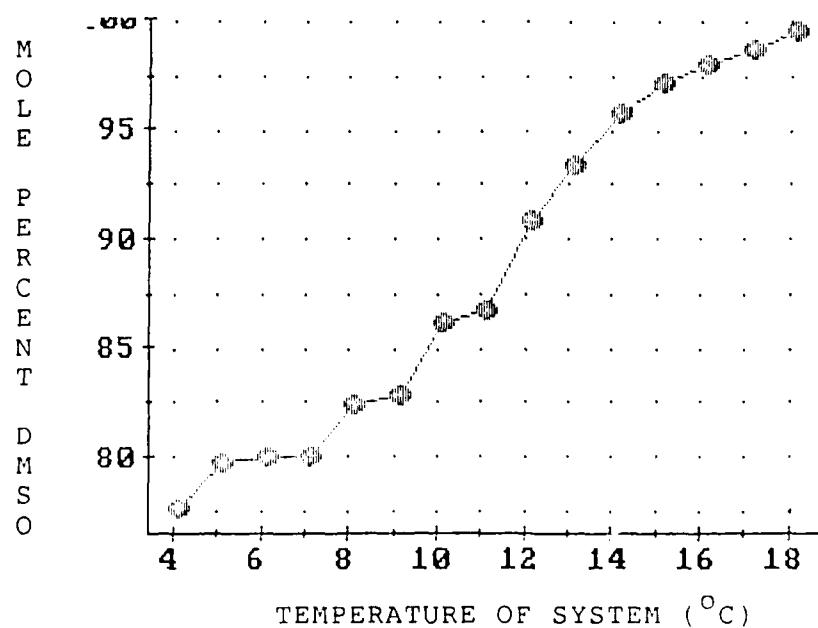
Figure 9: Change in DMSO composition for a
           heating rate of 6.0°C/hr.
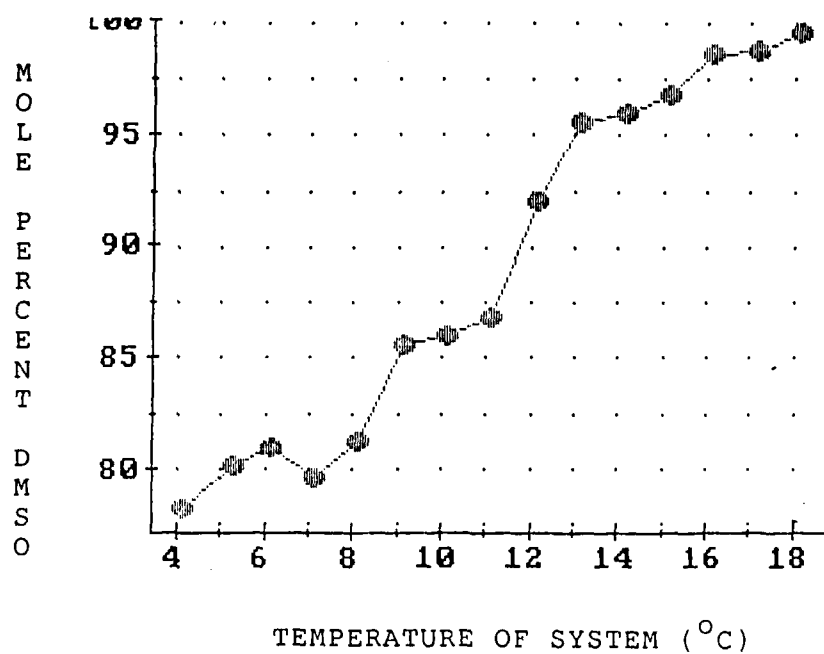
Figure 10: Change in DMSO composition for a
heating rate of 7.5°C/hr.
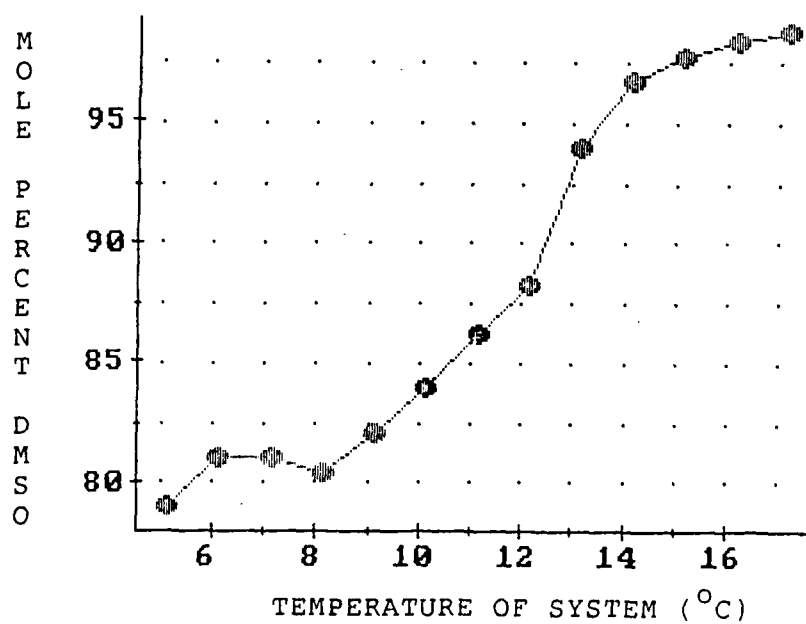
Figure 11: Change in DMSO composition for a
heating rate of 10.0°C/hr.

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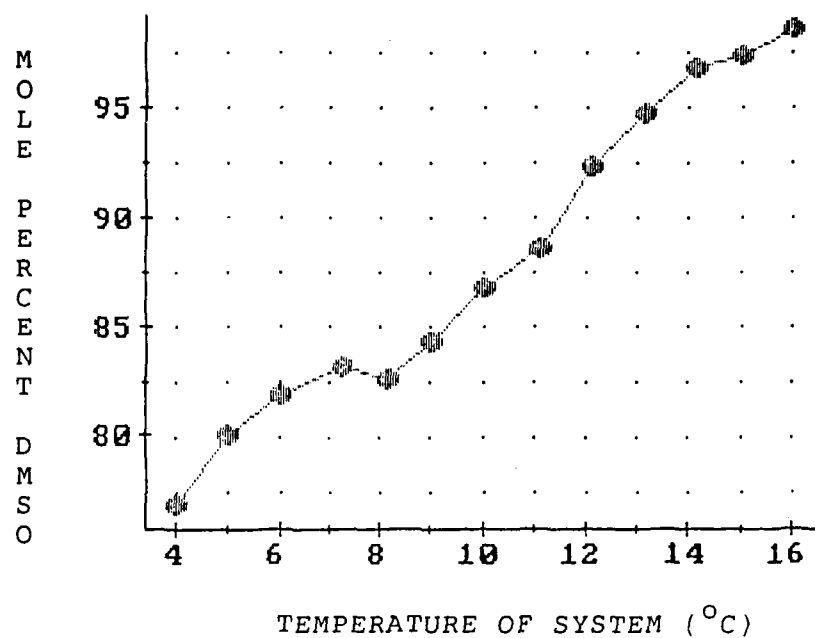
Figure 12: Change in DMSO composition for a heating rate of 11.0°C/hr.
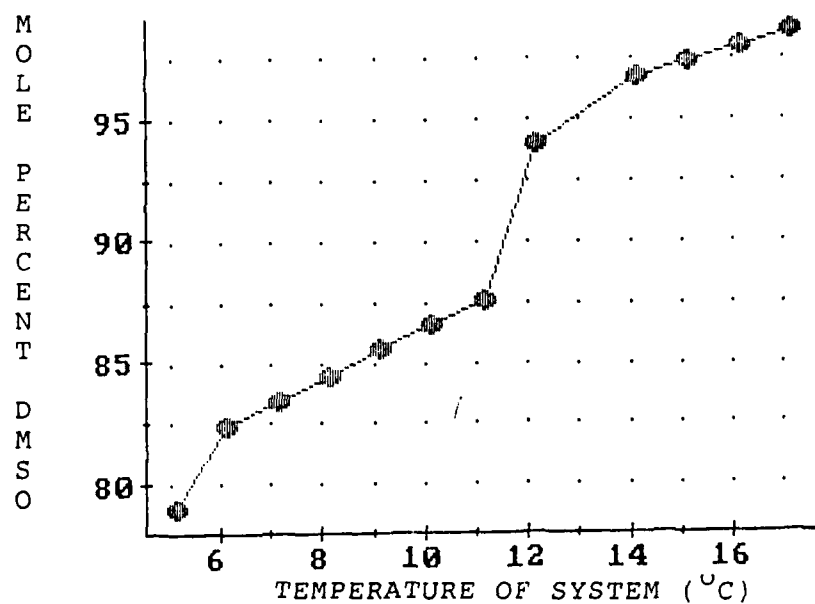
Figure 13: Change in DMSO composition for a heating rate of 14.0°C/hr.
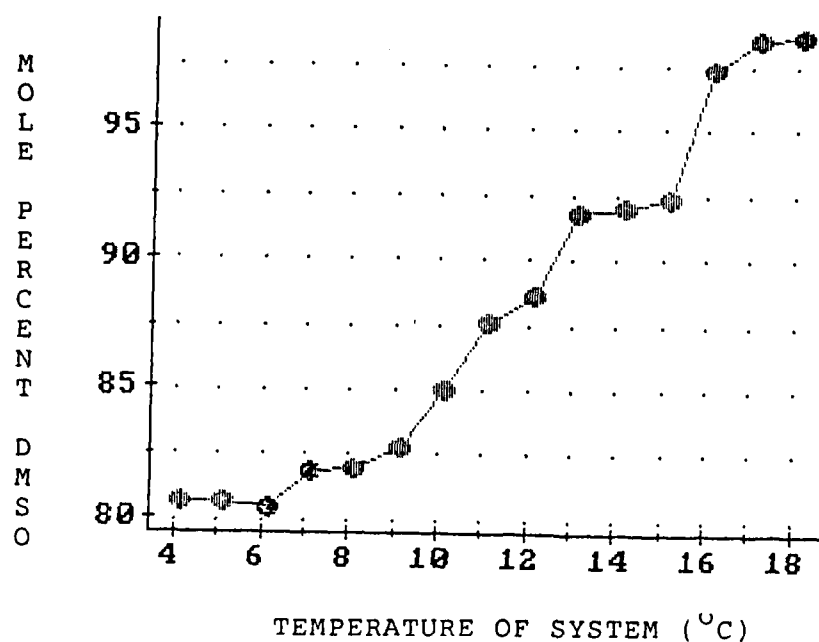
Figure 14:   Change in DMSO composition for a heating rate of 21.7°C/hr.
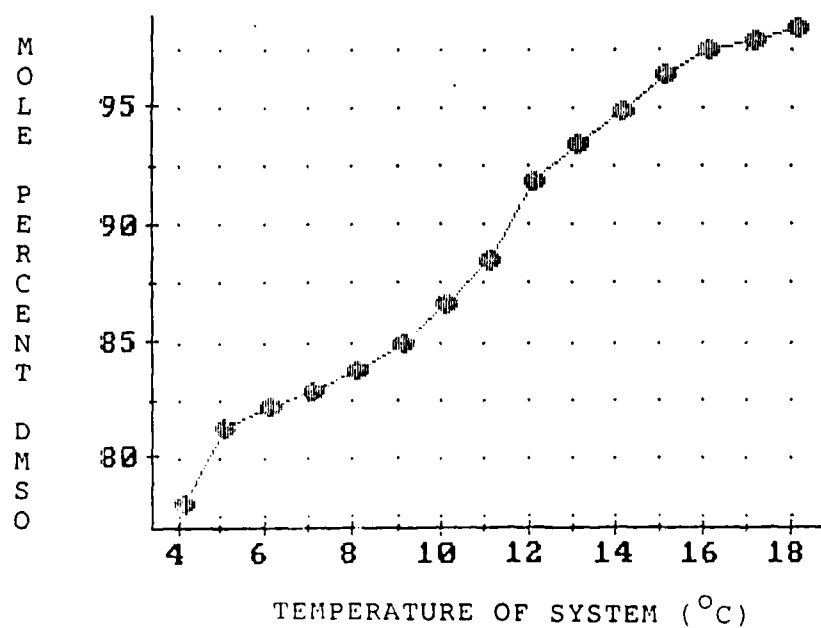
Figure 15:   Change in DMSO composition for a heating rate of 27.8°C/hr.
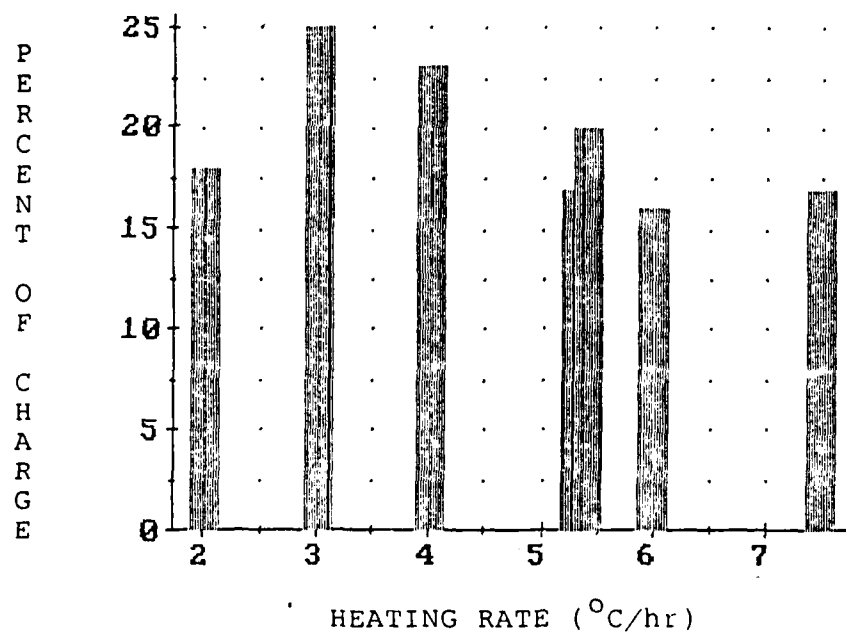
Figure 16: Comparision of amount of product for each
heating rate below 7.5°C/hr.
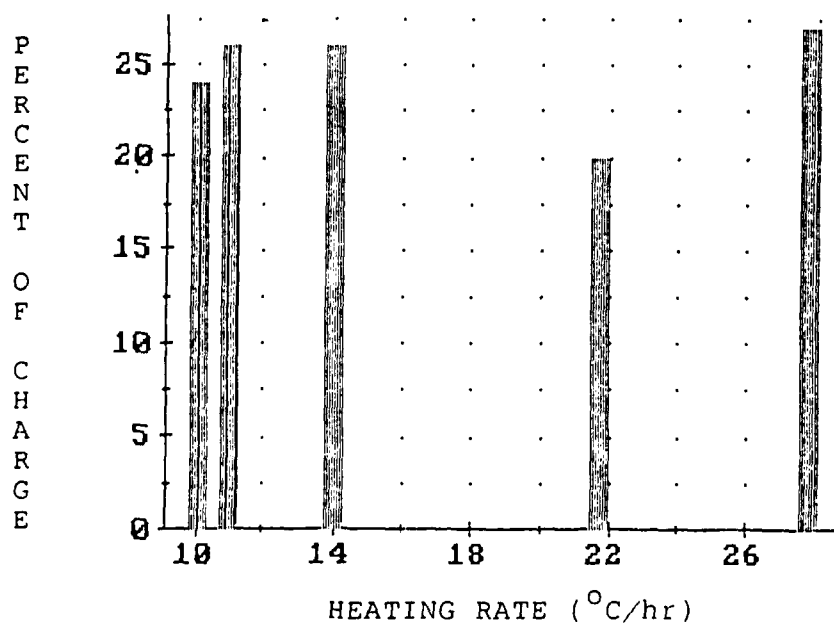
Figure 17: Comparision of amount of product for each
heating rate above 10.0°C/hr.

The amounts of product as a percentage of the initial charge for each heating rate are shown in Figures 16 and 17. The faster heating rates generally produced a larger amount of product than the slower ones. This could be due to the time required to perform the slower heating allowed more solid to melt. The heating rate with the largest amount of product was the fastest heating rate of 27.8 ^{O}C/hr. The composition of the product was 98.4 mole percent DMSO for this heating rate.

Therefore, there must be a compromise between the amount of product and the desired composition. The decision on this compromise must be made by the producer. For this experiment, the composition of the product was considered more important than the amount of product. The economics of the process were not considered for this experiment. This would change the importance of the composition of the product because of the time involved to produce the product.

(2) To develop a program to control the cooling and heating process.

The control of the equipment was accomplished by trial and error. By performing the process, a basic scheme was developed to produce the approximate cooling and heating rates. The basic schemes were then refined to produce the desired rates for the process.

Initially, the fine-tuned scheme was used to control the equipment without the system in the crystallizer. This created problems because the air reacted differently to the changing temperatures produced by the control scheme than the system did. Once this was realized, the control scheme was used with the system in the crystallizer. This procedure produced the programs that eventually controlled the equipment during the processs. The programs developed for this experiment are listed in Appendix C. The method for using the programs for this experiment is in Appendix D.

The purpose of the programs was to control the rate at which the temperature of the system decreased or increased. As mentioned earlier, it was attempted to maintain a constant cooling of the system from trial to trial. The desired heating rate was varied for each trial to study its effect of the degree of separation achieved. Figure 18 compares the actual heating rate with the desired heating rate entered into the program at the beginning of the heating step. The programs generally produced a heating rate which was very close to the desired rate. The heating rate was determined by calculating the time required for the temperature of the system to increase three degrees. The average

heating rate was determined by this method because it allowed time for the program to control the temperature oscillations. The temperature oscillations were produced by the equipment attempting to reach the desired temperature and overshooting it. The oscillations were usually greater for the slower heating rates.

(3) To develop a mathematical model to represent the cooling and heating process which occurs during melt crystallization.

The ability of the mathematical model to represent the process was not determined. This was because the thermodynamic conductivity for solid DMSO was unavailable. By observing the process, it was determined that the progession of the freezing interface was very slow. The temperature determined by the thermocouple between the crystallizer wall and the coil did not decrease to the freezing temperature very rapidly. This would suggest that system was still liquid at that position. Therefore, the solid-liquid interface had not progessed to that point. The experimental data of the temperature of the system as the cooling progressed is in Appendix B.
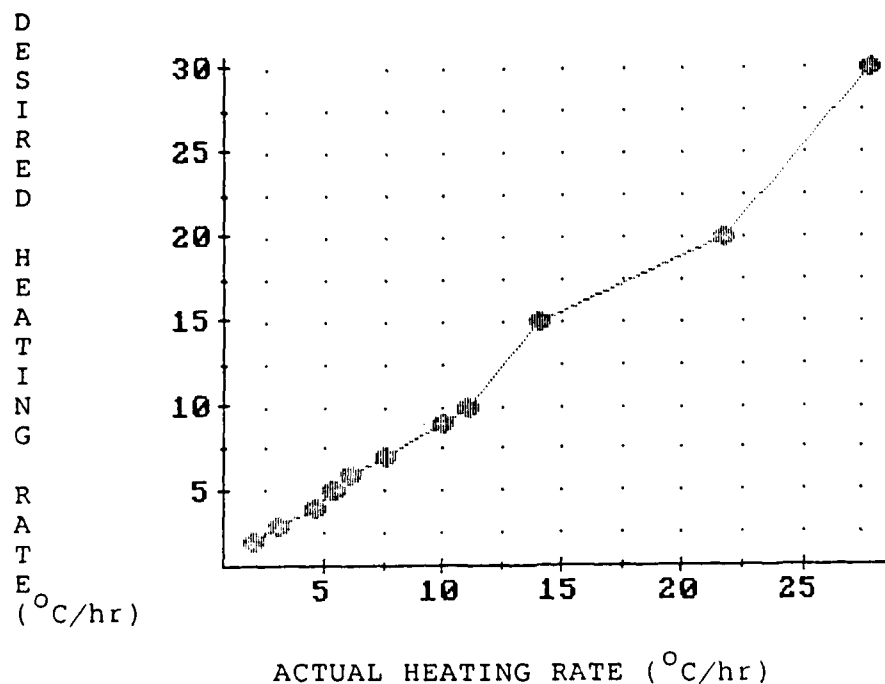
Figure 18: Comparison of the desired heating rate in $^{\circ}$C/hr with the actual heating rate in $^{\circ}$C/hr.

(4) To compare the energy requirements for the separation of the DMSO-Water system with the minimum energy requirements for the same separation.

The energy requirement for each trial are shown in Table 1.(The energy requirement for the heating rate of 11.0 $^{\circ}$C/hr was not determined because the composition of the initial charge was not determined.) The energy requirements were calculated based on the following assumptions. The DMSO-water system is an ideal

solution and Raoult's law is applicable. The
thermodynamic efficiency calculated from the minimum
energy requirement and the actual energy requirement
for each trial are in Appendix J. The heating rate
with the highest thermodynamic efficiency of 0.23 was
27.8 $^\circ$C/hr. The other heating rates had thermodynamic
efficiencies between 0.11 and 0.22. The general trend
was that the faster heating rates had a higher
thermodynamic efficiency. However, the slower heating
rates did not follow any apparent trend for that group
of heating rates below 7.5 $^\circ$C/hr. It was originally
intended to compare the energy requirements of melt
crystallization with those of distillation but this was
not accomplished. However, if the thermodynamic
efficiency of a distillation process were determined,
the energy requirements for both processes could then
be compared.

HEATING RATE($^\circ$C/hr)	ENERGY REQUIREMENTS (kcal)
2.0	4.6
3.0	6.4
4.5	5.6
5.3	6.3
5.4	4.4
6.0	5.7
7.5	4.6
10.0	4.6
11.0	---
14.0	4.7
21.7	4.0
27.8	5.1

Table 1: The energy requirements for each trial of
this experiment.

CONCLUSIONS

The conclusions for this experiment are as follows:

(1) The composition of the product did not change significantly as the heating rate decreased. This could signify that it is not as important to the separation process for this system as originally thought.

(2) Generally, the higher heating rates, $10^{\circ}C/hr$ and higher, produced a larger amount of product than the lower heating rates. This was because more time was required for the slower heating steps which allowed more solid to melt.

(3) The cooling rate is a very important factor in a melt crystallization process for the DMSO-water system used for this experiment. It was attempted to keep the cooling rate constant from trial to trial. However, the cooling rate was slower for a few trials because the room temperature was higher. This caused a decrease in the ability in the working fluid to remove

energy from the system. For the final trial, the cooling rate was not controlled to see the effects of a rapid cooling. However, the limitations of the equipment and the higher room temperature prevented the *cooling rate from* being much higher than previous trials.

(4) The equipment was able to freeze between 60 to 71% of the initial charge. *The amount frozen depended on* the temperature of the room. The higher the room temperature the more difficult it was for the working fluid to freeze the charge.

(5) Theoretically, the mathematical model should represent the process very closely. Unfortunately, this could not be proven because the thermal conductivity for solid DMSO was not known. Also, as the system froze, a layer of crystals formed over the top of the system preventing the measurement of the progression of the solid-liquid interface.

(6) The computer programs developed for this experiment were able to adequately control the equipment to produce the desired cooling rate and the various heating rates. There were some oscillations in the temperatures being controlled but these were dampened out quickly enough for the system not to be greatly disturbed.

(7)   The amount of energy required to separate the
DMSO-water system by melt crystallization was between
4.4 and 6.3 kcal for the trials in this experiment.
Also, the thermodynamic efficiency for the process
ranged from 0.11 to 0.23.

Recommendations

There are several recommendations which should be considered before repeating this experiment with the same system and equipment.

(1)   The cooling process should be considered as the more important process. For this project, the varied parameter was the heating rate. The results revealed that for any heating rate the product was essentially the same in composition. Therefore, changing the heating rate from trial to trial did not have a significant effect on the results. The liquid drawn off after the slow cooling process had a composition of about twice the amount of water than the original charge. For this reason, it seems apparent that the cooling process is very important to this melt crystallization process.

(2)   The physical properties of the solid for the major component should be found before any system is chosen. These properties are required to solve any mathematical scheme to model the process. And for any scale up calculations to be performed a mathematical model is required.

(3) The equiment should include a reservoir of about five gallons to replace the two stabilizer tanks which would reduce the temperature oscillations in the working fluid produced by the heater and the cooler. The capacity of the reservoir should be large enough to damp the oscillations, but not too large to afford a rapid change in temperature when required.

(4) A bypass around the heater would reduce the temperature shock from the heater. The bypass valve should not be activated by the same signal which activates the valve that allows flow through the heater. This would allow the working fluid to through both the heater and the bypass. This would allow easier control of the slow heating rates.

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APPENDIX A

DATA:

10 FEB 86   Gradient œ 11°C/hr

Bottle No.	Empty	With Sample	Sample
		Weight (gms)	
1	116.180	165.400	49.220
2	115.950	149.190	33.240
3	113.750	141.710	27.960
4	110.380	137.740	27.360
5	111.075	126.170	15.095
6	114.880	137.000	22.120
7	116.640	140.240	23.600
8	117.040	171.170	54.130
9	112.680	181.000	68.320
10	113.250	162.420	49.170
11	111.870	177.125	65.255
12	116.060	210.115	94.055
13	117.040		
14	115.095	423.120	190.985

Sample	Water Area%	Water Mole%	DMSO Area%	DMSO Mole%
1	8.6	23.1	91.4	76.9
2	7.1	19.8	92.9	80.2
3	6.4	18.0	93.6	82.0
4	6.0	16.8	94.0	83.2
5	6.2	17.4	93.8	82.6
6	5.0	15.7	95.0	84.3
7	4.8	13.2	95.2	86.8
8	4.3	11.4	95.7	88.6
9	3.2	7.6	96.8	92.4
10	2.4	5.2	97.6	94.8
11	1.7	3.2	98.3	96.8
12	1.5	2.6	98.5	97.4
13&14	0.8	1.3	99.2	98.7
23	–	–	–	
24	6.9	19.4	93.1	80.6

13 FEB 86   Gradient œ 10°C/hr

| Bottle No. | Weight (gms) | | Sample |
	Empty	With Sample	
1	115.780	215.120	99.340
2	115.540	151.980	36.440
3	113.340	131.040	17.700
4	110.310	125.850	15.540
5	118.890	128.215	9.325
6	114.350	132.070	17.720
7	116.350	143.930	27.580
8	117.020	155.865	38.845
9	112.290	227.150	114.860
10	112.980	218.180	105.200
11	111.550	194.930	83.380
12	115.780	169.460	53.680
13	116.640	158.050	41.410
14	115.090	187.230	72.140

| Sample | Water | | DMSO | |
	Area%	Mole%	Area%	Mole%
1	7.6	21.0	92.4	79.0
2	6.8	19.0	93.2	81.0
3	6.8	19.0	93.2	81.0
4	7.0	19.6	93.0	80.4
5	6.4	18.0	93.6	82.0
6	5.7	16.0	94.3	84.0
7	5.0	13.8	95.0	86.2
8	4.4	11.7	95.6	88.3
9	2.7	6.0	97.3	94.0
10	1.7	3.2	98.3	96.8
11	1.3	2.2	98.7	97.8
12	1.0	1.6	99.0	98.4
13	0.9	1.4	99.1	98.6
14	0.7	1.2	99.3	98.8
23	4.0	10.0	96.0	90.0
24	7.4	20.4	92.6	79.6

<u>15 Feb 86</u>   <u>Gradient</u> œ 14.0°C/hr

Bottle No.	Weight (gms)		
	<u>Empty</u>	<u>With Sample</u>	<u>Sample</u>
1	115.870	194.070	78.200
2	115.580	176.060	60.480
3	113.530	139.450	25.920
4	110.110	133.330	23.220
5	110.780	137.270	26.490
6	114.430	135.500	21.070
7	116.400	136.365	19.965
8	116.805	159.940	43.135
9	112.560	191.510	78.950
10	113.060	165.890	52.830
11	111.640	227.600	115.960
12	115.865	199.060	83.195
13	116.860	165.940	49.080

Sample	Water		DMSO	
	<u>Area%</u>	<u>Mole%</u>	<u>Area%</u>	<u>Mole%</u>
1	7.6	21.0	92.4	79.0
2	6.3	17.6	93.7	82.4
3	5.9	16.6	94.1	83.4
4	5.6	15.6	94.4	84.4
5	5.2	14.4	94.8	85.6
6	4.9	13.4	95.1	86.6
7	4.6	12.4	95.4	87.6
8	2.7	6.0	97.3	94.0
9	1.7	3.2	98.3	96.8
10	1.6	2.8	98.4	97.2
11	1.5	2.6	98.5	97.4
12	1.2	2.0	98.8	98.0
13	0.8	1.3	99.2	98.7
23	3.8	9.4	96.2	90.6
24	7.3	20.2	92.7	79.8

18 FEB 86   Gradient œ 7.5°C/hr

Bottle No.	Empty	Weight (gms) With Sample	Sample
1	115.820	176.340	60.520
2	115.570	169.260	53.690
3	113.440	134.830	21.390
4	110.150	131.040	20.890
5	110.690	141.060	30.370
6	114.370	135.995	21.625
7	116.370	144.260	27.890
8	116.740	140.880	24.140
9	112.380	177.410	65.030
10	112.990	180.710	67.720
11	111.500	171.830	60.330
12	115.820	184.420	68.600
13	116.690	237.835	121.145
14	115.070	215.410	100.340
15	115.215	241.130	125.915

Sample	Water Area%	Mole%	DMSO Area%	Mole%
1	8.0	21.8	92.0	78.2
2	7.1	19.8	92.9	80.2
3	6.8	19.0	93.2	81.0
4	7.4	20.4	92.6	79.6
5	6.7	18.8	93.3	81.2
6	5.2	14.4	94.8	85.6
7	5.1	14.0	94.9	86.0
8	4.8	13.2	95.2	86.8
9	3.3	8.0	96.7	92.0
10	2.2	4.4	97.8	95.6
11	2.0	4.0	98.0	96.0
12	1.7	3.2	98.3	96.8
13	0.9	1.4	99.1	98.6
14	0.7	1.2	99.3	98.8
15	0.3	0.4	99.7	99.6
23	3.6	8.8	96.4	91.2
24	7.4	20.4	92.6	79.6

20 FEB 86   Gradient œ 6.0°C/hr

Bottle No.	Empty	Weight (gms) With Sample	Sample
1	115.790	234.690	118.900
2	115.510	135.210	19.700
3	113.435	137.085	23.650
4	110.090	155.230	45.140
5	110.800	122.455	11.655
6	114.370	142.410	28.040
7	116.340	138.165	21.825
8	116.790	140.410	23.620
9	112.300	163.990	51.690
10	113.030	156.770	43.740
11	111.565	172.570	61.005
12	115.785	190.310	74.525
13	116.910	179.640	62.730
14	114.730	182.510	67.780
15	115.135	241.220	126.085
16	116.530	244.740	128.210
17	114.620	142.860	28.240

Sample	Water Area%	Water Mole%	DMSO Area%	DMSO Mole%
1	8.3	22.4	91.7	77.6
2	7.3	20.2	92.7	79.8
3	7.2	20.0	92.8	80.0
4	7.2	20.0	92.8	80.0
5	6.3	17.6	93.7	82.4
6	6.1	17.2	93.9	82.8
7	5.0	13.8	95.0	86.2
8	4.8	13.2	95.2	86.8
9	3.7	9.2	96.3	90.8
10	2.9	6.6	97.1	93.4
11	2.1	4.2	97.9	95.8
12	1.6	2.8	98.4	97.2
13	1.2	2.0	98.8	98.0
14	0.8	1.3	99.2	98.7
15	0.3	0.4	99.7	99.6
16	Same as Sample 15			
17	Same as Sample 15			
23	3.9	9.8	96.1	90.2
24	7.7	21.2	92.3	78.8

26 FEB 86   Gradient œ 5.3°C/hr

Bottle No.	Weight (gms)		
	Empty	With Sample	Sample
1	115.670	192.750	77.080
2	115.490	140.065	24.575
3	113.325	172.135	58.810
4	110.060	126.470	16.410
5	114.410	154.020	39.610
6	116.290	156.280	39.990
7	116.730	167.740	51.010
8	112.320	140.545	28.225
9	112.920	197.570	84.650
10	111.580	211.000	99.420
11	115.755	213.550	97.795
12	116.655	192.720	76.065
13	114.800	173.800	59.000
14	114.910	132.985	18.075

Sample	Water		DMSO	
	Area%	Mole%	Area%	Mole%
1	7.7	21.2	92.3	79.8
2	6.9	19.4	93.1	80.6
3	6.0	16.8	94.0	83.2
4	5.3	14.6	94.7	85.4
5	5.2	14.4	94.8	85.6
6	2.6	5.8	97.4	94.2
7	2.0	4.0	98.0	96.0
8	2.9	6.6	97.1	93.4
9	1.9	3.6	98.1	96.4
10	1.5	2.6	98.5	97.4
11	0.6	1.0	99.4	99.0
12	0.4	0.7	99.6	99.3
13	0.2	0.3	99.8	99.7
14	0.2	0.3	99.8	99.7
23	3.8	9.4	96.2	90.6
24	6.7	18.8	93.3	81.2

1 MAR 86   Gradient œ 4.5°C/hr

Bottle No.	Weight (gms)		
	Empty	With Sample	Sample
1	115.830	250.325	134.495
2	115.490	170.100	54.610
3	113.350	141.655	28.305
4	110.150	149.100	38.950
5	110.760	134.450	23.690
6	114.370	171.660	57.290
7	116.370	139.885	23.515
8	116.765	158.730	41.965
9	112.330	164.210	51.880
10	112.970	182.980	70.010
11	111.600	233.740	122.140
12	115.800	191.235	74.435
13	116.630	185.100	68.470

Sample	Water		DMSO	
	Area%	Mole%	Area%	Mole%
1	7.4	20.4	92.6	79.6
2	7.3	20.2	92.7	79.8
3	6.6	18.4	93.4	81.6
4	6.1	17.2	93.9	82.8
5	5.7	16.0	94.3	84.0
6	5.6	15.6	94.4	84.4
7	5.6	15.6	94.4	84.4
8	4.6	12.4	95.4	87.6
9	3.0	7.0	97.0	93.0
10	3.3	8.0	96.7	92.0
11	1.6	2.8	98.4	97.2
12	1.0	1.6	99.0	98.4
13	0.5	0.8	99.5	99.2
23	4.0	10.0	96.0	90.0
24	7.4	20.4	92.6	79.6

5 MAR 86   Gradient œ 3.0°C/hr

Bottle No.	Empty	Weight (gms) With Sample	Sample
1	115.830	201.120	85.290
2	115.570	142.400	26.830
3	113.370	146.170	32.800
4	110.080	138.010	27.930
5	110.740	149.870	39.130
6	114.340	123.380	9.040
7	116.310	164.910	48.600
8	116.670	157.290	40.620
9	112.300	155.850	43.550
10	113.015	160.060	47.045
11	111.610	121.630	10.020
12	115.850	135.310	19.460
13	116.610	175.630	59.020
14	114.820	175.630	60.810
15	114.910	250.500	135.590

Sample	Water Area%	Water Mole%	DMSO Area%	DMSO Mole%
1	8.2	22.2	91.8	77.8
2	7.8	21.4	92.2	78.6
3	7.6	21.0	92.4	79.0
4	6.2	17.4	93.8	82.6
5	6.3	17.8	93.7	82.2
6	5.7	16.0	94.3	84.0
7	5.2	14.4	94.8	85.6
8	4.5	12.0	95.5	88.0
9	3.7	9.2	96.3	90.8
10	2.9	6.6	97.1	93.4
11	2.6	5.8	97.4	94.2
12	1.8	3.4	98.2	96.6
13	1.6	2.8	98.4	97.2
14	0.9	1.4	99.1	98.6
15	0.6	1.0	99.4	99.0
23	3.9	9.8	96.1	90.2
24	7.9	21.6	92.1	78.4

7 MAR 86   Gradient œ 2.0°C/hr

Bottle No.	Empty	Weight (gms) With Sample	Sample
1	115.810	145.370	29.560
2	115.490	203.140	87.650
3	113.420	232.460	119.040
4	109.980	177.960	67.980
5	110.690	170.535	59.845
6	114.390	152.230	37.840
7	116.260	187.790	71.530
8	116.750	160.435	43.685
9	112.300	148.580	36.280
10	112.895	179.450	66.555
11	111.580	238.870	127.290
12	115.760	147.600	31.840
13	115.585	172.950	57.365
14	114.800	216.660	101.860

Sample	Water Area%	Mole%	DMSO Area%	Mole%
1	7.4	20.4	92.6	79.6
2	7.8	21.4	92.2	78.6
3	7.4	20.4	92.6	79.6
4	6.6	18.4	93.4	81.6
5	6.3	17.8	93.7	82.2
6	6.0	16.8	94.0	83.2
7	5.9	16.6	94.3	83.4
8	5.2	14.4	94.8	85.6
9	4.4	11.6	95.6	88.4
10	2.7	6.0	97.3	94.0
11	2.0	4.0	98.0	96.0
12	1.1	1.8	98.9	98.2
13	0.7	1.2	99.3	98.8
14	0.4	0.7	99.6	99.3
23	4.0	10.0	96.0	90.0
24	6.0	16.8	94.0	83.2

11 MAR 86   Gradient œ 21.7^{O}C/hr

Bottle No.	Weight (gms)		
	Empty	With Sample	Sample
1	115.810	164.680	48.870
2	115.480	201.520	86.040
3	113.280	174.600	61.320
4	110.070	153.900	43.830
5	110.710	150.720	40.010
6	114.380	153.030	38.650
7	116.340	154.170	37.830
8	114.660	161.900	47.240
9	112.350	170.780	58.430
10	112.950	175.350	62.400
11	111.540	162.020	50.480
12	115.770	169.525	53.755
13	116.660	198.440	81.780
14	114.800	172.300	57.530
15	114.930	161.770	46.840

Sample	Water		DMSO	
	Area%	Mole%	Area%	Mole%
1	6.9	19.4	93.1	80.6
2	6.9	19.4	93.1	80.6
3	7.0	19.6	93.0	80.4
4	6.5	18.2	93.5	81.8
5	6.4	18.0	93.6	82.0
6	6.1	17.2	93.9	82.8
7	5.4	15.0	94.6	85.0
8	4.6	12.4	95.4	87.6
9	4.3	11.4	95.7	88.6
10	3.4	8.2	96.6	91.8
11	3.3	8.0	96.7	92.0
12	3.2	7.6	96.8	92.4
13	1.5	2.6	98.5	97.4
14	0.9	1.4	99.1	98.6
15	0.8	1.3	99.2	98.7
23	4.2	11.0	95.8	89.0
24	6.4	18.0	93.6	82.0

13 MAR 86   Gradient œ 27.8°C/hr

Bottle No.	Empty	Weight (gms) With Sample	Sample
1	115.790	184.960	69.170
2	115.465	174.300	58.835
3	113.330	144.125	30.795
4	110.080	133.280	23.200
5	110.770	133.850	23.080
6	114.370	137.745	23.375
7	116.260	141.850	25.590
8	114.630	141.500	26.870
9	112.310	142.580	30.270
10	112.920	144.630	31.710
11	111.550	149.440	37.890
12	115.800	164.670	48.870
13	116.595	163.630	47.035
14	114.700	156.425	41.725
15	114.920	211.020	96.100

Sample	Water Area%	Mole%	DMSO Area%	Mole%
1	8.1	22.0	91.9	78.0
2	6.7	18.7	93.3	81.3
3	6.3	17.8	93.7	82.2
4	6.1	17.2	93.9	82.8
5	5.8	16.2	94.2	83.8
6	5.4	15.0	94.6	85.0
7	4.9	13.4	95.1	86.6
8	4.4	11.6	95.6	88.4
9	3.4	8.2	96.6	91.8
10	2.9	6.6	97.1	93.4
11	2.4	5.2	97.6	94.8
12	1.9	3.6	98.1	96.4
13	1.5	2.6	98.5	97.4
14	1.3	2.2	98.7	97.8
15	1.0	1.6	99.0	98.4
23	4.4	11.6	95.6	88.4
24	7.9	21.6	92.1	78.4

15 MAR 86   Gradient œ 5.4°C/hr

Bottle No.	Empty	Weight (gms) With Sample	Sample
1	115.745	218.490	102.745
2	115.570	201.750	86.180
3	113.400	156.330	42.930
4	110.090	135.140	25.050
5	110.830	131.995	21.165
6	114.450	169.730	55.280
7	116.400	136.460	20.060
8	114.710	144.250	29.540
9	112.420	201.540	89.120
10	112.950	189.980	77.030
11	111.620	180.900	69.280
12	115.820	168.730	52.910
13	116.660	175.920	59.260
14	114.775	197.695	82.920

Sample	Water Area%	Mole%	DMSO Area%	Mole%
1	7.7	21.2	92.3	78.8
2	7.5	20.8	92.5	79.2
3	6.4	18.0	93.6	82.0
4	7.1	19.8	92.9	80.2
5	6.3	17.8	93.7	82.2
6	6.2	17.4	93.8	82.6
7	5.6	15.6	94.4	84.4
8	5.0	13.8	95.0	86.2
9	4.4	11.6	95.6	88.4
10	2.3	4.8	97.7	95.2
11	1.6	2.8	98.4	97.2
12	1.7	3.1	98.3	96.9
13	0.8	1.3	99.2	98.7
14	0.5	1.0	99.5	99.0
23	4.2	11.0	95.8	89.0
24	6.4	18.0	93.6	82.0

APPENDIX B

EXPERIMENTAL TRIALS

Temperatures in ^{O}C

Date: 4 FEB 86   Gradient œ $11.0^{O}C/hr$

Time	Temperature in	
	Crystallizer	Tap Water
START FREEZING	Charge= 1600 ml = 1754 gm	
09:22	25.000	25.250
09:37	21.750	32.375
09:52	18.375	31.625
10:07	16.375	29.125
10:22	14.625	17.875
10.37	11.750	16.875
0.52	12.125	17.000
11:07	12.000	16.750
11:22	11.875	17.375
11:37	11.750	17.000
11:52	11.375	17.250
12:07	11.000	17.125
12:22	10.625	17.000
12:37	10.125	17.500
12:52	9.750	8.875
13:07	9.000	8.750
13:22	8.500	9.125
13:37	7.875	9.125
13:52	7.375	9.125
14:07	6.875	9.000
14:22	6.625	9.250
14:37	6.125	9.125
14:52	5.500	8.875
15:22	4.250	8.625
15:37	4.125	8.625
15:52	3.875	8.875
16:39	3.250	9.375
START MELTING	Drawn Off= 520 ml = 570 gm(32% of charge)	
16:49	3.500	9.000
SAMPLE 1		
16:52	4.000	19.625
SAMPLE 2		
16:57	5.000	19.625
SAMPLE 3		
17:00	6.000	13.625
SAMPLE 4		
17:06	7.250	9.250

SAMPLE 5 17:11	8.125	9.250
SAMPLE 6 17:22	9.000	20.125
SAMPLE 7 17:29	10.000	20.500
SAMPLE 8 17:37	11.125	37.000
SAMPLE 9 17:42	12.125	52.125
SAMPLE 10 17:45	13.125	52.500
SAMPLE 11 17:48	14.125	48.375
SAMPLE 12 17:52	15.000	40.625
SAMPLE 13 & 14 18:01	16.000	43.125

Remaining Liquid= 415 ml = 455 gm(26% of charge)
Total time = 10 hrs 39 mins

Date: __12 FEB 86__ __Gradient__ œ $10.0^{\circ}C/hr$

Time	Temperature in	
	Crystallizer	Tap Water
START FREEZING	Charge= 1600 ml = 1754 gm	
09:53	23.625	30.125
10:08	20.875	30.125
10:23	17.000	29.625
10:38	14.500	29.250
10:53	12.875	28.375
11:08	11.875	21.500
11:12	11.750	21.375
11:27	11.875	16.000
11:42	11.750	16.500
11:57	11.500	16.375
12:12	11.125	16.250
12:27	10.750	10.375
12:42	9.750	9.875
12:57	9.000	10.000
13:12	8.125	10.000
13:27	7.375	9.250
13:42	6.750	9.125
13:57	6.000	9.750
14:12	5.375	10.000
14:27	4.875	9.750
14:42	4.375	9.375

14:57	3.875	9.000
15:12	3.500	9.250
15:45	5.625	9.500
16:00	5.125	8.000
16:15	4.875	7.625
16:30	4.750	7.625
16:45	4.875	8.125
17:00	4.500	8.500

START MELTING Drawn Off= 550 ml = 603 gm(34% of charge)

17:29	4.375	9.000
SAMPLE 1		
17:34	5.125	19.875
SAMPLE 2		
17:38	6.125	23.625
SAMPLE 3		
17:41	7.125	19.375
SAMPLE 4		
17:45	8.125	16.250
SAMPLE 5		
17:51	9.125	10.750
SAMPLE 6		
18:00	10.125	10.250
SAMPLE 7		
18:10	11.125	10.125
SAMPLE 8		
18:22	12.125	17.875
SAMPLE 9		
18:34	13.125	46.500
SAMPLE 10		
18:40	14.125	47.000
SAMPLE 11		
18:44	15.125	47.875
SAMPLE 12		
18:48	16.125	47.625
SAMPLE 13		
18:51	17.125	47.375

Remaining Liquid= 390 ml = 427 gm(24% of charge)
Total time = 10 hrs 38 mins

Date: 14 FEB 86   Gradient $\propto$ 14.0°C/hr

Time	Temperature in	
	Crystallizer	Tap Water
START FREEZING	Charge= 1600 ml = 1754 gm	
09:11	23.125	28.750
09:26	19.750	32.500
09:41	16.625	30.125
09:56	14.625	30.625
10:11	12.875	22.375
10:26	11.875	23.000
10:41	12.000	21.875
10:56	11.875	23.000
11:11	11.750	22.750
11:26	11.500	22.250
11:41	11.375	8.625
11:56	10.750	8.500
12:11	10.000	8.250
12:26	9.500	8.000
12:41	8.875	8.125
12:56	8.875	8.375
13:11	8.250	11.875
13:26	8.250	12.500
13:41	7.625	12.250
13:56	7.125	12.375
14:11	6.750	12.500
14:26	6.375	12.875
14:41	5.875	12.875
14:56	5.500	12.750
15:11	5.125	8.750
15:26	4.500	8.750
15:41	3.875	8.250
15:56	4.250	8.250
16:11	4.125	8.500
START MELTING	Drawn Off= 560 ml = 614 gm(35% of charge)	
16:19	4.375	8.750
SAMPLE 1		
16:23	5.125	35.250
SAMPLE 2		
16:27	6.125	36.125
SAMPLE 3		
16:30	7.125	36.375
SAMPLE 4		
16:32	8.125	29.875
SAMPLE 5		
16:36	9.125	25.000
SAMPLE 6		
16:40	10.125	25.000
SAMPLE 7		
16:47	11.125	28.875

```
SAMPLE 8
16:53                12.125                48.125
SAMPLE 9
16:56                14.125                48.625
SAMPLE 10
17:00                15.125                34.000
SAMPLE 11
17:08                16.125                33.250
SAMPLE 12
17:13                17.125                33.125
Remaining Liquid= 420 ml = 460 gm(26% of charge)
Total time = 10 hrs 2 mins
```

Date: 17 FEB 86   Gradient œ 7.5°C/hr

Time	Temperature in		
	Crystallizer	Tap Water	Jacket
START FREEZING	Charge= 1600 ml = 1754 gm		
10:41	22.250	36.500	22.625
10:56	19.125	31.250	20.000
11:11	16.125	30.625	15.125
11:26	14.125	29.875	12.875
11:41	12.625	31.625	12.625
11:56	11.875	30.375	11.750
12:11	11.250	29.375	11.125
12:26	10.875	29.375	10.500
12:41	10.500	21.875	10.125
12:56	11.875	23.250	12.125
13:11	12.125	22.375	10.125
13:26	12.125	22.250	11.500
13:41	12.125	22.000	10.500
13:56	12.000	21.750	10.625
14:11	11.875	21.625	11.000
14:26	11.750	8.500	9.250
14:41	11.375	8.500	8.500
14:56	11.250	8.500	9.625
15:11	11.125	14.750	10.625
15:14	11.125	19.625	9.000
15:29	10.875	19.750	8.375
15:44	10.500	8.875	3.250
15:59	9.875	9.000	3.875
16:14	9.250	9.125	4.750
16:29	8.750	9.250	2.750
16:44	8.125	9.375	3.375
16:59	7.750	9.250	3.750
17:14	7.625	9.500	3.625
17:29	7.000	9.375	3.500

17:44	6.750	9.000	3.375
17:59	6.500	9.125	3.000
18:14	6.125	11.375	3.625
18:29	6.125	9.500	4.250
18:44	5.625	9.500	4.750
18:59	5.250	9.500	4.750
19:32	4.375	9.500	5.750
19:47	4.250	9.500	3.125
20:02	4.125	9.250	3.125
20:17	4.000	9.125	2.750
20:32	3.875	9.250	3.125

START MELTING Drawn Off= 550 ml = 603 gm(34% of charge)

20:38	3.875	9.375

SAMPLE 1

20:43	4.125	23.000

SAMPLE 2

20:47	5.250	23.250

SAMPLE 3

20:50	6.125	17.750

SAMPLE 4

20:54	7.125	9.750

SAMPLE 5

21:08	8.125	9.500

SAMPLE 6

21:13	9.125	9.375

SAMPLE 7

21:18	10.125	9.500

SAMPLE 8

21:29	11.125	9.500

SAMPLE 9

21:42	12.125	16.500

SAMPLE 10

21:46	13.125	16.625

SAMPLE 11

21:52	14.125	12.875

SAMPLE 12

22:05	15.125	29.375

SAMPLE 13

22:15	16.125	35.875

SAMPLE 14

22:21	17.125	35.750

SAMPLE 15

22:27	18.125	35.375

Remaining Liquid= 270 ml = 296 gm(17% of charge)
Total time = 13 hrs 46 mins

Date: __19 FEB 86__ Gradient œ 6.0^{O}C/hr

Time	Temperature in		
	Crystallizer	Tap Water	Jacket
START FREEZING	Charge= 1600 ml = 1754 gm		
10:17	47.125	22.125	51.750
10:32	16.750	20.000	12.250
10:47	12.375	19.750	11.250
11:02	11.625	19.625	8.250
11:17	11.500	19.125	7.500
11:32	11.000	18.875	7.625
11:47	10.750	19.875	7.875
12:02	10.500	19.500	7.500
12:17	10.125	20.125	8.000
12:32	9.875	19.625	7.625
12:47	9.750	19.500	7.750
13:02	9.500	19.500	7.375
13:17	9.375	19.250	7.750
13:32	9.250	18.625	7.250
13:47	9.125	12.000	5.375
14:02	8.500	12.000	4.000
14:17	7.750	12.250	3.750
14:32	7.375	12.375	4.125
14:47	7.125	8.875	2.625
15:02	6.375	8.625	2.250
15:17	5.750	8.500	2.000
15:32	4.875	8.250	0.875
15:47	5.375	8.500	5.125
16:02	5.125	8.625	2.375
16:17	4.375	8.750	2.375
16:32	3.625	8.875	2.250
START MELTING Drawn Off= 500 ml = 548 gm(31% of charge)			
16:38	3.250	9.000	
SAMPLE 1			
16:45	4.125	13.250	
SAMPLE 2			
16:47	5.125	13.375	
SAMPLE 3			
16:51	6.125	13.250	
SAMPLE 4			
17:08	7.125	13.250	
SAMPLE 5			
17:11	8.125	13.125	
SAMPLE 6			
17:29	9.125	17.250	
SAMPLE 7			
17:35	10.125	17.500	
SAMPLE 8			
17:45	11.125	17.375	
SAMPLE 9			
17:58	12.125	21.250	

```
SAMPLE 10
18:07               13.125        21.250
SAMPLE 11
18:20               14.125        21.000
SAMPLE 12
18:28               15.125        21.000
SAMPLE 13
18:38               16.125        20.625
SAMPLE 14
18:51               17.125        20.250
SAMPLE 15
19:14               18.125        36.500
Remaining Liquid= 250 ml = 274 gm(16% of charge)
Total time = 8 hrs 57 mins
```

Date: 25 FEB 86   Gradient œ 5.3°C/hr

Time	Temperature in		
	Crystallizer	Tap Water	Jacket
START FREEZING	Charge= 1600 ml = 1754 gm		
10:51	23.000	19.875	------
11:06	14.250	18.875	------
11:21	11.875	18.375	------
11:36	12.000	18.875	------
11:51	11.875	18.500	------
12:06	11.500	9.125	------
12:21	10.750	14.000	------
12:36	10.375	14.625	------
12:51	9.875	14.375	------
13:06	9.125	14.500	------
13:21	8.500	14.750	------
13:36	7.750	14.500	------
13:51	7.125	14.625	------
14:06	6.625	10.625	------
14:21	5.750	10.375	------
14:35	5.875	9.750	2.500
14:50	5.375	9.750	7.625
15:05	5.375	10.125	2.625
15:20	4.875	9.750	7.500
15:35	5.000	10.000	2.625
15:50	4.750	9.875	7.250
16:05	4.750	10.000	2.375

```
START MELTING Drawn Off= 645 ml = 707 gm(40% of charge)
16:17               5.000         9.500
SAMPLE 1
16:24               6.125         9.625
SAMPLE 2
16:30               7.125         9.625
```

```
SAMPLE 3
16:52                    8.125          10.250
SAMPLE 4
16:55                    9.125          10.375
SAMPLE 5
17:22                   10.125          14.125
SAMPLE 6
17:26                   11.125          14.125
SAMPLE 7
17:30                   12.125          14.000
SAMPLE 8
17:37                   13.125          14.125
SAMPLE 9
18:08                   14.125          13.875
SAMPLE 10
18:15                   15.125          13.875
SAMPLE 11
18:26                   16.125          14.000
SAMPLE 12
18:44                   17.125          14.125
SAMPLE 13
18:54                   18.125          14.375
```

Remaining Liquid= 270 ml = 296 gm(17% of charge)
Total time = 8 hrs 3 mins

Date: 28 FEB 86   Gradient œ 4.5°C/hr

Time	Temperature in		
	Crystallizer	Tap Water	Jacket
START FREEZING	Charge= 1600 ml = 1754 gm		
08:49	23.500	20.125	24.500
09:04	14.750	16.000	12.625
09:19	10.625	15.250	6.875
09:34	11.500	14.500	5.000
09:49	10.500	13.750	4.250
10:04	9.875	13.625	4.000
10:19	9.250	10.125	2.750
10:34	8.875	10.125	7.000
10:49	8.625	10.500	2.875
11:04	8.000	10.875	5.625
11:19	7.500	10.875	2.875
11:34	6.625	11.125	8.125
11:49	6.500	11.500	3.000
12:04	5.750	11.750	3.375
12:19	5.125	11.375	2.750
12:34	4.500	11.625	3.000
12:49	4.125	11.375	2.750

```
13:43                    4.750          11.500          1.750
13:58                    4.750           8.625          6.750
14:13                    4.625           8.500          5.125
14:28                    5.125           8.375          2.625
14:43                    4.750           8.125          8.125
START MELTING Drawn Off= 520 ml = 570 gm(32% of charge)
14:47                    5.000           8.250          2.875
SAMPLE 1 .
14:58                    6.125           8.250          9.875
SAMPLE 2
15:20                    7.125           9.125         17.625
SAMPLE 3
15:25                    8.125           9.750         11.500
SAMPLE 4
15:45                    9.125          10.125         20.875
SAMPLE 5
15:51                   10.125          10.375         12.250
SAMPLE 6
16:12                   11.125          10.500         24.000
SAMPLE 7
16:18                   12.125          10.625         13.750
SAMPLE 8
16:42                   13.125          10.750         22.875
SAMPLE 9
16:49                   14.125          10.750         17.625
SAMPLE 10
17:11                   15.125          10.375         24.375
SAMPLE 11
17:19                   16.125          10.250         27.625
SAMPLE 12
17:37                   17.125          10.375         24.500
SAMPLE 13
17:47                   18.125          10.250         25.375
Remaining Liquid= 360 ml = 395 gm(23% of charge)
Total time = 8 hrs 58 mins
```

Date: 4 MAR 86 Gradient œ 3.0°C/hr

Time	Temperature in		
	Crystallizer	Tap Water	Jacket
START FREEZING	Charge= 1600 ml = 1754 gm		
10:32	22.750	21.125	19.625
10:47	14.875	18.375	12.250
11:02	11.125	17.500	7.750
11:17	11.625	17.125	6.125
11:32	11.000	16.250	5.375
11:47	10.375	17.375	5.375
12:02	10.000	17.000	5.375
12:17	9.625	16.375	5.250
12:32	9.250	16.250	5.000
12:47	8.875	15.750	4.875
13:02	8.125	8.500	4.375
13:17	8.250	8.750	3.125
13:32	7.750	8.375	7.750
13:47	7.750	8.500	3.750
14:02	7.625	11.875	4.000
14:17	7.000	11.500	4.750
15:01	6.125	11.625	4.375
15:16	6.250	8.125	3.500
15:31	5.625	8.625	7.500
15:46	5.625	8.625	3.125
15:58	5.500	8.500	5.375
16:13	5.250	11.375	5.250
16.28	5.500	12.125	3.875
16:43	4.875	12.250	3.125
16:58	4.250	12.625	3.250
17:13	3.875	12.750	3.250
17:28	3.750	12.875	3.750
START MELTING Drawn	Off= 540 ml = 592 gm(34% of charge)		
17:50	3.500	12.500	5.875
SAMPLE 1			
17:55	4.125	12.500	10.875
SAMPLE 2			
17:59	5.125	12.750	6.125
SAMPLE 3			
18:26	6.125	12.875	7.750
SAMPLE 4			
18:50	7.125	12.875	11.500
SAMPLE 5			
19:20	8.125	13.125	14.750
SAMPLE 6			
19:24	9.125	13.250	10.750
SAMPLE 7			
19:53	10.125	13.125	16.000
SAMPLE 8			
20:23	11.125	13.125	25.000

```
SAMPLE 9
20:53              12.125        12.875        23.500
SAMPLE 10
21:23              13.375        12.875        20.500
SAMPLE 11
21:31              14.125        13.000        27.000
SAMPLE 12
21:39              15.125        13.250        18.375
SAMPLE 13
22:14              16.125        13.125        28.750
SAMPLE 14
22:23              17.125        13.375        31.000
SAMPLE 15
22:51              18.125        13.000        29.500
Remaining Liquid= 400 ml = 438 gm(25% of charge)
Total time = 12 hrs 19 mins
```

Date: 6 MAR 86   Gradient œ $2.0^{o}C/hr$

Time	Temperature in		
	Crystallizer	Tap Water	Jacket
START FREEZING	Charge= 1600 ml = 1754 gm		
10:01	23.750	22.000	19.500
10:16	15.250	19.875	14.250
10:31	10.500	15.125	7.750
10:46	11.375	14.625	4.750
11:01	11.000	14.375	4.375
11:16	10.125	14.500	4.250
11:31	9.500	14.250	3.750
11:46	8.750	14.875	4.000
12:01	8.125	14.750	4.000
12:16	7.500	14.125	4.000
12:31	6.875	14.250	3.875
12:46	6.250	14.500	4.000
13:01	5.750	14.500	4.000
13:16	5.375	12.125	4.000
13:31	5.000	12.125	3.125
13:46	4.500	11.875	2.750
14:01	4.000	11.875	2.625
14:12	3.750	11.875	2.500
14:27	3.500	11.375	2.625
14:42	3.500	11.250	8.375
14:57	4.000	11.250	2.750
15:12	3.750	11.875	2.625
START MELTING	Drawn Off= 460 ml = 504 gm(29% of charge)		
15:15	3.875	11.125	8.375

SAMPLE 1
15:18   4.125   11.250   13.375
SAMPLE 2
15:25   5.125   11.125   6.750
SAMPLE 3
16:20   6.125   11.750   18.500
SAMPLE 4
16:52   7.125   11.875   19.125
SAMPLE 5
17:24   8.125   12.000   21.250
SAMPLE 6
17:29   9.125   12.000   11.125
SAMPLE 7
18:23   10.125   12.250   22.750
SAMPLE 8
18:54   11.125   12.250   24.250
SAMPLE 9
19:30   12.125   12.125   26.000
SAMPLE 10
19:36   13.125   12.125   18.000
SAMPLE 11
20:56   15.125   12.125   24.875
SAMPLE 12
21.23   16.125   12.000   23.750
SAMPLE 13
21:56   17.250   11.750   17.000
SAMPLE 14
22:27   18.125   11.875   28.250
Remaining Liquid= 290 ml = 318 gm(18% of charge)
Total time = 12 hrs 26 mins

Date: 10 MAR 86   Gradient œ $21.7^{O}C/hr$

Time	Temperature in		
	Crystallizer	Tap Water	Jacket
START FREEZING	Charge= 1600 ml = 1754 gm		
10:24	24.500	26.750	26.375
10:39	16.250	21.125	13.125
10:54	11.125	13.000	6.375
11:09	11.250	12.625	4.250
11:24	11.125	12.375	3.375
11:39	10.500	12.125	3.500
11:54	9.375	12.250	3.375
12:09	8.500	12.250	3.375
12:24	7.500	12.125	3.375
12:39	6.625	12.125	3.375
12:54	5.875	12.000	3.250

13:09	5.125	12.500	3.500
13:46	3.250	12.250	2.750
14:01	3.250	12.375	4.375
14:16	3.750	12.500	3.750
14:31	3.750	12.375	3.750
14:46	3.625	12.250	4.000
14:58	3.375	12.125	3.125

START MELTING Drawn Off= 540 ml = 592 gm(34% of charge)

15:07	3.375	12.375	5.875
SAMPLE 1			
15:12	4.125	12.375	16.500
SAMPLE 2			
15:16	5.125	20.250	20.875
SAMPLE 3			
15:19	6.125	21.875	24.500
SAMPLE 4			
15:21	7.125	21.750	27.375
SAMPLE 5			
15:24	8.125	21.750	29.375
SAMPLE 6			
15:26	9.125	21.750	30.875
SAMPLE 7			
15:28	10.125	21.750	32.125
SAMPLE 8			
15:30	11.125	21.750	32.375
SAMPLE 9			
15:32	12.125	21.625	27.625
SAMPLE 10			
15:33	13.125	21.625	19.625
SAMPLE 11			
15:36	14.125	21.625	16.875
SAMPLE 12			
15:44	15.125	21.375	19.250
SAMPLE 13			
15:51	16.125	21.250	29.250
SAMPLE 14			
15:54	17.125	21.250	31.375
SAMPLE 15			
15:57	18.125	21.250	32.750

Remaining Liquid= 320 ml = 351 gm(20% of charge)
Total time = 5 hrs 33 mins
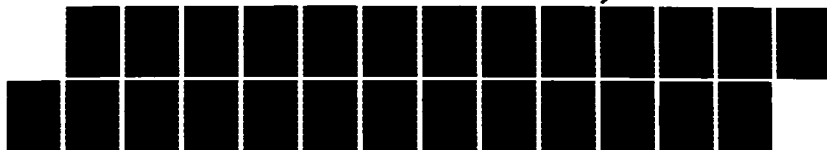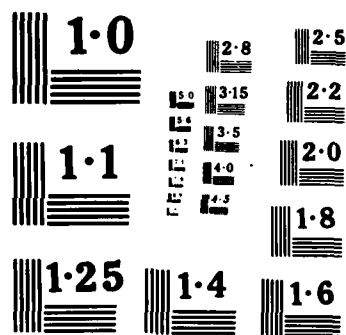
```
START MELTING Drawn Off= 530 ml = 581 gm(33% of charge)
15:29                3.000        13.250         3.000
SAMPLE 1
15:30                4.125        13.500        10.250
SAMPLE 2
15:55                5.125        13.375        12.000
SAMPLE 3
16:02                6.125        13.375        22.500
SAMPLE 4
16:05                7.125        13.375        15.625
SAMPLE 5
16:09                8.125        13.375        12.000
SAMPLE 6
16:45                9.125        13.500        24.375
SAMPLE 7
16:50               10.125        13.375        27.125
SAMPLE 8
16:55               11.125        13.000        21.000
SAMPLE 9
17:30               13.125        13.375        25.875
SAMPLE 10
17:37               14.125        13.375        29.250
SAMPLE 11
17:43               15.125        13.625        21.125
SAMPLE 12
17:58               16.125        13.625        20.500
SAMPLE 13
18:14               17.125        13.625        28.250
SAMPLE 14
18:25               18.125        13.625        27.375
Remaining Liquid= 320 ml = 351 gm(20% of charge)
Total time = 7 hrs 54 mins
```

APPENDIX C

Program: FREEZ

This program is used to control the freezing process of the DMSO-Water system. Lines 10 through 90 dimensionalize, initialize, and prints the initial temperatures in various locations of the equipment. The array, T, is dimensionalized to eleven which is the number of thermocouple channels in the A/D converter. The subroutine at line 4000, called in line 15, initializes and starts Timer1 in the Aim 65. In lines 20 through 35, the final temperature(FT), the time between temperature changes(Q), and the approximate freezing point of the system are entered. Line 90 calls the subroutine at line 5000 which prints the initial time, the temperature in the crystallizer, the tap water, and the working fluid entering the coil inside the crystallizer. Line 95 calls the main subroutine at line 3020 which activates the I/O ports to the various control mechanisms in the equipment. Line 100 tells the user to load MELT1 to begin the heating sequence. Line 105 leaves the I/O ports activated to not allow any premature heating of the system.

```
10     DIM T(11)
15     GOSUB 4000
20     FT=5.0
30     Q=1.0
35     FP=11.75
89     PRINT! "START"
90     GOSUB 5000
95     GOSUB 3020
100    PRINT! "LOAD MELTING PROGRAM"
105    POKE 40960,134
110    END
```

The subroutine which begins at line 2000 reads the temperature from the A/D converter. Line 2000 puts the value of I into memory location 40209. The wait command, also in that line, allows the A/D converter time to retrieve the signal from the specified thermocouple. Line 2010 tells the computer to examine the information at the address of 40210 and 40211. In line 2020, three bytes of nonsense are eliminated from the information in 40211. The information is converted to a integer and then to a real number. This leaves

two bits in Y1 as 0 to 3°C. Therefore, X1 in line 2025 has a range of 4 to 512°C which is the upper limit for the temperature. X1 and Y1 are added together to give the temperature for the specified thermocouple. Line 2035 checks T(I) and insures that it is inside the range for the temperatures.

```
2000 POKE 40209,I: WAIT 40209,32,32
2010 X=PEEK(40210): Y=PEEK(40211)
2020 Z%=Y/8: Y1=Z/8
2025 X1=X*4
2030 T(I)=X1 + Y1
2035 IF T(I)>512 THEN T(I)=T(I) - 1024: RETURN
2040 RETURN
```

The subroutine at line 3020 controls the flow of the working fluid and the heater to reach the desired temperature for the system. In line 3020, a value is sent to address 40962 and it determines which of the eight ports are output. The value in the next address, 40960, determines which ports are active. The ports are number 0,1,2,3,4,5,6,7 and each can be activated to open or close a valve, turn the heater on, or turn the alarm off. A "1" activates port 0 which is the cooler and cooler bypass valves, a "2" activates port 1 which is the heat exchanger and tap water valves, and a "4" activates port 2 which is the heat exchanger bypass valve. A "64" activates port 6 which turns on the heater. A "128" activates port 7 which turns off the alarm. For numerous commands to be performed, the numbers can be added together and the sum put in address 40960. So, "132" activates port 2 which opens the heat exchanger bypass valve and port 7 which turns the alarm off. N in line 3050 is the temperature increment used to decrease the temperature inside the crystallizer.

Lines 3065 through 3140 are used to compare the change in temperatures of the working fluid and the crystallizer. Once the temperatures have been compared and various values assigned J%, H%, and K%, the total value, L%, is put into address 40960. J% is for the cooler and cooler bypass valves. H% is for the heat exchanger, heat exchanger bypass, and tap water valves. K% is for the heater. Lines 3116 through 3118 are a time delay to allow the changes in the valves and the heater to have an effect. Lines 3120 through 3140 compare the values of the time to determine if it is time to print the temperatures of the crystallizer, tap water, and the working fluid entering the coil. Also, if the final temperature has been reached inside the crystallizer, the program will move to line 3142. In

the section, it is attempted to hold the temperature in the crystallizer at the final temperature for one hour. Once the hour is completed, the program returns to line 100.

```
3020 POKE 40962,255: POKE 40960,132
3050 N=-0.5
3060 ML=M
3065 I=11: GOSUB 2000
3070 TEMP=T(11) + N
3080 I=0: GOSUB 2000
3082 IF T(0)<(TEMP-1.0) THEN J%=1
3083 IF T(0)>=TEMP THEN J%=0
3084 IF (T(0) - TL)>0 THEN J%=0
3085 IF T(0)>FP AND T(11)>17.0 THEN J%=0
3086 IF T(0)<FP  AND T(11)>17.0 THEN J%=1
3089 IF T(11)<=FP THEN J%=0
3090 IF T(0)<=TEMP THEN H%=2
3091 IF (T(0) - TL)<0 AND T(0)<(TEMP + 0.625) THEN H%=2
3092 IF (T(0) - TL)>0 THEN H%=6
3094 IF T(0)>=TEMP THEN H%=6
3095 IF (T(0) - TL)<0 THEN K%=64
3096 IF (T(0) - TL)>=0 THEN K% = 0
3098 L%= H% + J% + K% + 128
3100 POKE 40960,L%
3110 PRINT T(0), TEMP
3115 TL = T(0)
3116 FOR A=1 TO 100
3117 A=A+1
3118 NEXT A
3120 M=PEEK(4031)
3121 IF M0>45 AND (M - M0)=15 THEN GOSUB 5000
3122 IF M0>=45 AND (M - M0)=-45 THEN GOSUB 5000
3125 I=11: GOSUB 2000
3130 IF T(11)<(FT+0.125) THEN GOTO 3142
3135 IF (M - ML)=Q OR (M - ML)=Q - 60 THEN GOTO 3060
3140 GOTO 3080
3142 H=PEEK(4030)
3145 HL=H: M1=M
3150 I=0: GOSUB 2000
3155 J%=0
3160 IF T(0)<(FT - 0.5) THEN H%=2
3161 IF T(0)>(FT - 0.5) THEN H%=6
3162 IF (T(0) - TL)<0 THEN H%=6
3165 IF (T(0) - TL)<0 THEN K%=64
3166 IF (T(0) - TL)=>0 THEN K%=0
3170 FOR A=1 TO 100
3171 A=A+1
3172 NEXT A
3175 L%=H% + J% + K% + 128
3180 POKE 40960,L%
```

```
3182 M=PEEK(4031)
3185 IF M0<45 AND (M - M0)=15 THEN GOSUB 5000
3186 IF M0>=45 AND (M - M0)=-45 THEN GOSUB  5000
3190 PRINT T(0), T(11)
3200 TL=T(0)
3205 H=PEEK(4030)
3210 IF M=M1  AND (H - HL)=1 OR (H - HL)=-23 THEN GOTO
     3225
3220 GOTO 3150
3225 PRINT! "END FREEZING"
3230 RETURN
```

In lines 4000 through 4060, Timer1 in the Aim 65 is initialized and started. Line 4010 reads the time in hours, minutes, and seconds. Line 4020 puts these values in the correct address and 4030 through 4050 starts the clock.

```
4000 PRINT "ENTER PRESENT TIME"
4010 INPUT C1,C2,C3
4020 POKE 4030,C1: POKE 4031,C2: POKE 40302,C3: POKE
     4033,0
4030 POKE 40974,192: POKE 40971,64
4040 POKE 41984,194: POKE 41985,15
4050 POKE 40964,34: POKE 40965,244
4060 RETURN
```

As mentioned earlier, this subroutine reads the time and the signal from certain thermocouples and prints a hard copy of these values.

```
5000 I=11: GOSUB 2000
5010 I=8: GOSUB 2000
5015 I=0: GOSUB 2000
5020 H=PEEK(4030): M=PEEK(4031)
5030 PRINT! H;":";M;T(11);T(8);T(0)
5040 M0=M
5050 RETURN
```

Program: Melt1

This program is used to control the heating process of
the DMSO-Water system. It is very similar to FREEZ,
except the temperature increment is positive instead of
negative. Lines 10 through 160 are different from
those in FREEZ in that more arrays are dimensionalized
and the input of these variables are made possible.

```
10    DIM TF(2),T(11),GD(2)
15    GOSUB 4000
40    INPUT "# SEGMENTS";N: IF N>20 THEN N=20
50    FOR C=1 TO N: PRINT C
80    NPUT "FINAL T";TF(C)
85    INPUT "GRADIENT";GD(C): NEXT C
97    PRINT! "START MELTING": GOSUB 5000
100   C=0
110   C=C+1: TF=TF(C): GD=GD(C)
120   GOTO 200
130   PRINT! "END PART";C;"OF;N
140   IF C<N THEN 110
150   PRINT! "END SEQUENCE"
160   END
```

Lines 200 through 860 are similar to lines 3120
through 3230 except there is not an hour holding period
as in FREEZ.

```
200   X$="0"
210   MR=60/(2*GD): S=1
211   MR=INT(MR)
215   M0=PEEK(4031)
216   H=PEEK(4030): M=PEEK(4031)
225   I=11: GOSUB 2000
226   TL=T(11)
230   TL=TL+0.5: HL=H
235   M2=M
240   I=VAL(X$): GOSUB 2000: PRINT X$;T(I);T(11)
250   GET A$: IF A$<>"" THEN PRINT A$: GOSUB 1020
260   I=0: GOSUB 2000
270   I=11: GOSUB 2000
280   IF T(11)<=TL THEN GOTO 400
290   IF T(11)>TL THEN GOTO 500
400   IF T(11)<(TL - 0.375) THEN J%=1
410   IF T(11)<=(TL - 0.375) THEN J%=0
420   IF (T(0) - LT)>0 THE H%=0
430   IF (T(0) - LT)<=0 THEN H%=64
440   IF (T(0) - LT)>0 THE K%=2
450   IF (T(0) - LT)<=0 THEN K%=6
460   L%=128 + J% + H% + K%: GOTO 725
500   J%=0
```

```
510    IF T(11)>=(TL + 0.25) THEN H%=0
520    IF (T(0) - LT)<0 THEN H%=64
530    IF (T(0) - LT)>=0 THEN H%=0
540    IF (T(0) - LT)<0 THEN K%=2
550    IF (T(0) - LT)>=0 THEN K%=6
560    L%=128 + J% + H% + K%
725    POKE 40960,L%
730    FOR A=1 TO 100
750    A=A+1
760    NEXT A
790    LT=T(0)
800    M=PEEK(4031): H=PEEK(4030)
802    IF (M - M0)=15 OR (M - M0)=-45 THEN GOSUB 5000
805    IF MR=>60 OR (M2 + MR)=>60 THEN GOTO 230
810    IF M2 + MR<60 AND M=(M2 + MR) THEN GOTO 230
812    IF (H - HL)=1 OR (H - HL)=-23 AND M=(M2 + MR -60)
       THEN GOTO 230
830    IF T(11)>=TF THEN GOTO 130
860    GOTO 240
```

In lines 1020 through 1050, it is possible to
input various instructions from the keyboard. An "R"
sends the program to the next segment of the heating
process. A "B" tells the computer to read the signal
from thermocouple channel number 11. A "S" means a
sample is being taken and the time and various
temperatures need to be printed.

```
1020 IF A$="r" THEN GOTO 140
1030 IF A$="B" THEN A$="11"
1035 IF A$="S" THEN PRINT! "SAMPLE=";S: S=S + 1
1040 IF A$="S" THEN GOSUB 5000
1050 X$=A$: RETURN
```

The three subroutines at lines 2000, 4000, and
5000 are the same subroutine from FREEZ.

```
2000 POKE 40209,I: WAIT 40209,32,32
2010 X=PEEK(40210): Y=PEEK(40211)
2020 Z%=Y/8: Y1=Z/8
2025 X1=X*4
2030 T(I)=X1 + Y1
2035 IF T(I)>512 THEN T(I)=T(I) - 1024: RETURN
2040 RETURN

4000 PRINT "ENTER PRESENT TIME"
4010 INPUT C1,C2,C3
4020 POKE 4030,C1: POKE 4031,C2: POKE 40302,C3: POKE
     4033,0
4030 POKE 40974,192: POKE 40971,64
4040 POKE 41984,194: POKE 41985,15
```

```
4050 POKE 40964,34: POKE 40965,244
4060 RETURN

5000 I=11: GOSUB 2000
5010 I=8: GOSUB 2000
5015 I=0: GOSUB 2000
5020 H=PEEK(4030): M=PEEK(4031)
5030 PRINT! H;":";M;T(11);T(8);T(0)
5040 M0=M
5050 RETURN
```

Appendix D

The purpose of this appendix is to familiarize the reader with the steps required to perform an experimental trial on the equipment for this research. The programs mentioned in this appendix are discussed in Appendix C and the reader should return to Appendix C to answer any questions about them.

There are four operations discussed in this appendix and they are

1) Connecting the AIM
2) Loading a program
3) Thermocouple calibration
4) Using control programs and crystallizer operations

1) Connecting the AIM 65

A) Place the microcomputer in a position so that the ribbon cables from the A/D converter(on the right) and the alarm box(on the left) can reach the appropriate ports on the AIM 65.

B) Place the cassette recorder on the left of the microcomputer and next to the alarm box.

C) Connect the ribbon cables from the alarm and the A/D converter to the right and the left male plug on the AIM, respectivitly.

D) Connect the red(positive) and black(negative) wires from the power output of the AIM to the A/D converter.

E) Connect the Mic plug on the cassette recorder to the the Mic jack on the alarm box and the ear plug jack on the cassette recorder to the Mon jack on the alarm box.

F) Plug in the AIM and the cassette recorder to the power outlets underneath the top shelf.

G) Check all manual switches to insure they are in the off position.

H) Turn the main power switch to the on position.

I) Open either solenoid valve 0 or 1.

J) Check the red toogle switch under the right side of the AIM to insure it is in the back position possible which puts the microcomputer in BASIC.

K) Turn on the AIM.

L) Press "<cntl>" and "<print>" keys to turn the printer off.

M) Press M and then A002 to display the memory for that location.

N) Press "/" and type FF, <cr>. This puts FF into A002.
O) Repeat steps M) and N) but replace A002 and FF with A409 and 40.
P) Press 5 which puts the user in BASIC.
Q) Press <cr> for the next two questions.

2) Loading a program for a cassette tape.
A) After entering BASIC, type LOAD <cr>.
B) The microcomputer will display In=, type T and <space bar>. Then type the name of the program which must be five letters or less and the number of the cassette recorder, 1 or 2.
C) The tape should be before the beginning of the program; press <cr> on the AIM and PLAY on the cassette recorder.
D) Once the program has been loaded, the microcomputer will display a "^". Press STOP on the cassette recorder.
E) If the program did not load into memory, try again.

3) Calibrating the thermocouples.
A) Use a program which displays the temperature of each thermocouple.
B) Drain the working fluid from the equipment.
C) Remove each thermocouple from its fitting.
D) Use the range of temperatures expected for a ordinary trial. For this research, an ice bath and water at about 45°C were used.
E) Put a thermometer in each calibration bath to determine the actual temperature.
F) Place a thermocouple in the ice bath.
G) Above each converter channel are two small blue rectangular boxes, the one on the right is for the zero and the other is for the gain. Adjust the zero until the appropriate temperature is displayed for the ice bath. If the temperature is 511.875 or 512, then the thermocouple wire is broken or there is a bad connection.
H) Switch to the warm bath and adjust the gain until that appropriate temperature is displayed.
I) Repeat steps F), G) and H) for the remaining thermocouples.
J) Replace the thermocouples into the original fittings.

4) Using the control programs and crystallizer operations.

- A) Fill the crystallizer with the system.
- B) Load program FREEZ. (It is best to allow the A/D converter to warm up before using it; about two to three hours is appropriate.)
- C) Turn on the pump and the cooler.
- D) Adjust the hot and cold tap water flow rates to achieve the desired temperature.
- E) Type RUN <cr>. The program will request the time in hours, minutes, and seconds for a 24-hour clock. The program will control the equipment to slowly cool the system. This process will take from five to eight hours depending on the room temperature.
- F) Once the system is solid, drain off the remaining liquid, record the volume, and put some in a sample bottle for analysis.
- G) Load program MELT1.
- H) Type RUN <cr>.
- I) The program will request the time in hours, minutes, and seconds for a 24-hour clock. Then the program will request the "# of Segments", the "Final T", and the desired "Gradient".
- J) Weigh all the sample bottles before every trial. Take a sample every degree for each trial. About 16 to 20 bottles are required.
- K) For larger gradients, the tap water temperature may have to be adjusted to produce the more rapid temperature increase.
- L) The heating process can be stopped after the solid has melted below the thermocouple. At that time, turn on the hot water to full, turn off the cold water, and turn on the manual switch for the heater to completely melt the solid.

APPENDIX E

Equipment Specifications

Type	Specifications	Manufacturer	Model No.
A/D converter	$\pm 0.125^{\circ}C$	Motorola	M68MM15B
A/D extensions	$\pm 0.125^{\circ}C$	Motorola	M68MM15bEX
Cooler	3/4 hp	Heat-X	CCP-25
Crystallizer	1750 ml	Mr. Haak*	
Heater	1 Kw	Watlow	BCC8N1WC81
Housing – height = 11.5in. outside diameter = 1.875in.			
Heat exchanger	Coil – 8 ft. of 3/8 in. Copper		
Housing – height = 26.5in. outside diameter = 4.5in.			
Microcomputer	4K RAM	Rockwell	AIM 6500
Pump	1/12 hp, 3200 RPM 20 ft H_2O head	Grundfos	UP26-64
Rotameter tube	8 gpm max	Fisher-Porter	B6-35-10/27
Solenoid valves	Norm. Open	ASCO	8210C33
(125 psi max)	Norm. Closed	ASCO	8210C93
Surge tank	1 liter Stainless steel	Unkown	
Tape Recorder	Cassette	GE	3-5152A

Temperature Display	^{o}F	Omega Eng. Inc.	199
Temperature Stabilizer tanks	1134 ml PVC plastic	-----	
Thermocouples	Copper-Constantan		
Scale	1000 gm max	Sartorius	2254
GC	Thermal Conductivity Detector	Gow-Mac	550P
Data Acquisition System	----	Keithley	500
Personal Computer	----	IBM	5150

APPENDIX F

Physical Properties of DMSO

Molecular Weight	78.13 gm/mol
Boiling point at 760 mm Hg	$189^{\circ}C$ ($372^{\circ}F$)
Freezing point	$18.55^{\circ}C$ ($65.4^{\circ}F$)
Molal freezing point constant	$4.07^{\circ}C(mol)^{-1}(kg)^{-1}$
Density at $25^{\circ}C$	1.096 gm/cm^3
Specific heat at $29.5^{\circ}C$	0.47 ± 0.015 cal/gm $^{\circ}C$
Heat capacity (liq.), $25^{\circ}C$	0.47 cal/gm $^{\circ}C$
Heat of fusion	41.3 cal/g
Heat of vaporization at $70^{\circ}C$	11.3 kcal/mol
Heat of solution in water at $25^{\circ}C$	52 cal/g
Flash point (open cup)	$95^{\circ}C$ ($203^{\circ}F$)
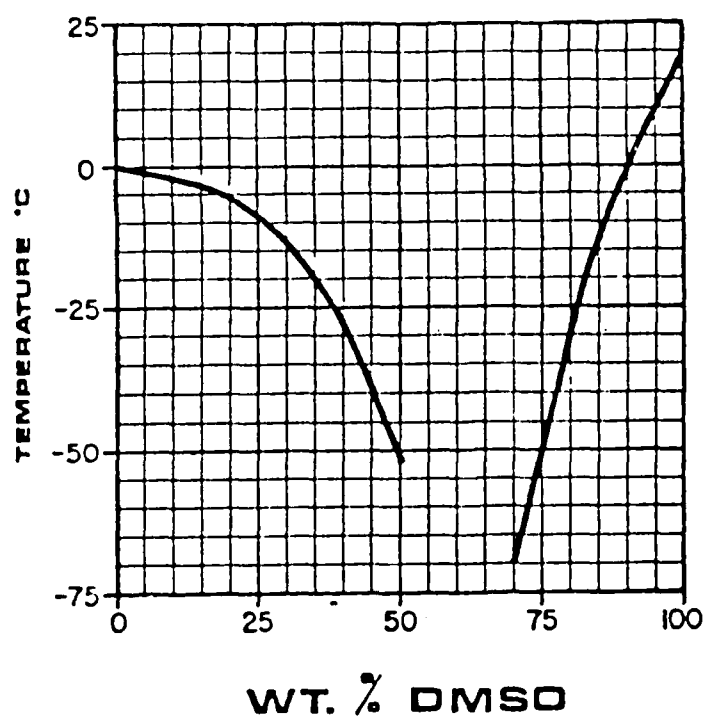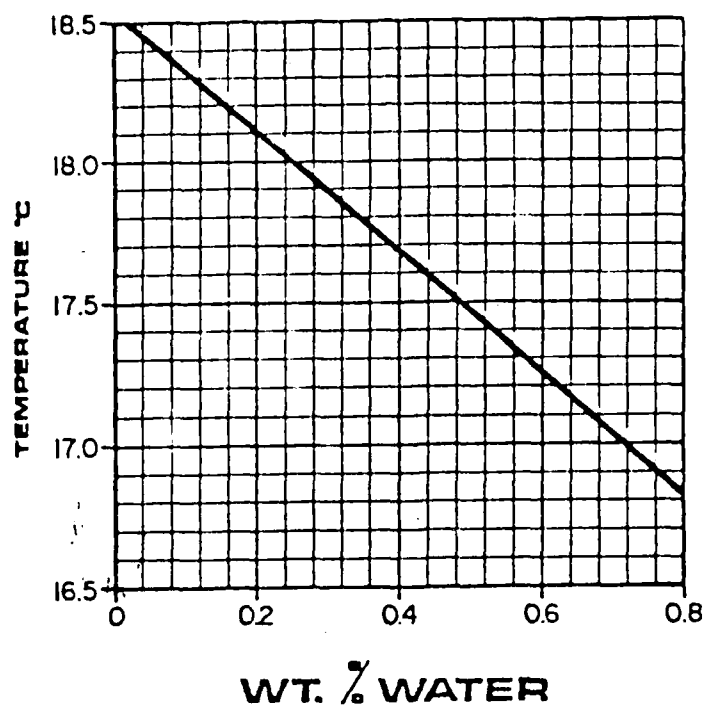
Figure A1: Freezing point curves for DMSO-Water
solutions.[2]

Appendix G

Gas Chromatograph Analysis

These specifications and procedure are from a technical
bulletin on DMSO wiitten by Crown Zellerbach.

Column specifications:

    Material of construction – stainless steel, 4 ft

    in length and with an outside diameter of 1/8

    inch.

    Packing – 15% FFAP (Varian Aerograph) on

    Chromosorb T (Johns-Mnaville), 40/60 mesh.

Gas Chromatograph Specifications:

    Column temperature – 150°C

    Detector temperature – 220°C

    Injector temperature – 210°C

    Carrier gas flow rate – 30 ml/min

Procedure:

    The sample size depends on the type of detector in

    the gas chromatograph. The retention time for

    DMSO for these conditions is about 12 minutes and

    for water about 30 seconds. Crown Zellerbach

    recommends a program time of 20 minutes if any

    other impurities are present.

Appendix H

There are several methods used to separate DMSO from water. The method to be discussed is used by Crown Zellerbach which is in the technical bulletin on DMSO. The typical feed for their process would be 10 to 20 percent DMSO. The limitations of the equipment used for this project would be unable to separate this type of mixture because of the mixture's low freezing point, which would be between -10 to -50°C.

The process used by Crown Zellerbach includes two vacuum distillation steps. The first column removes the less volatile impurities and produces the DMSO-Water system. The second column fractionally distills the solution to produce pure DMSO as the bottoms. The operating pressure for the columns is about 100 mm Hg which allows for the use of 85 psig steam and normally available cooling water.[1]
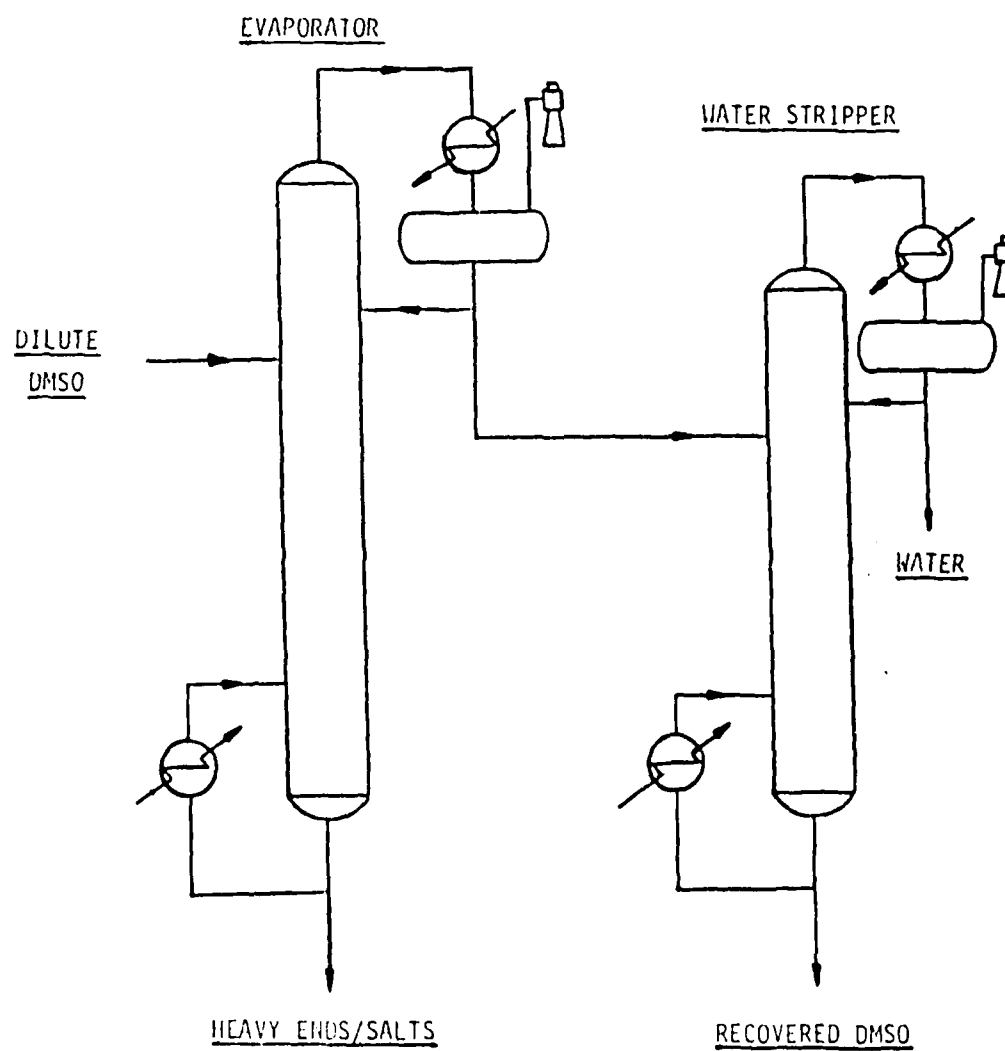
DMSO RECOVERY FROM AQUEOUS SOLUTIONS

Figure A2: A schematic diagram of the distillation
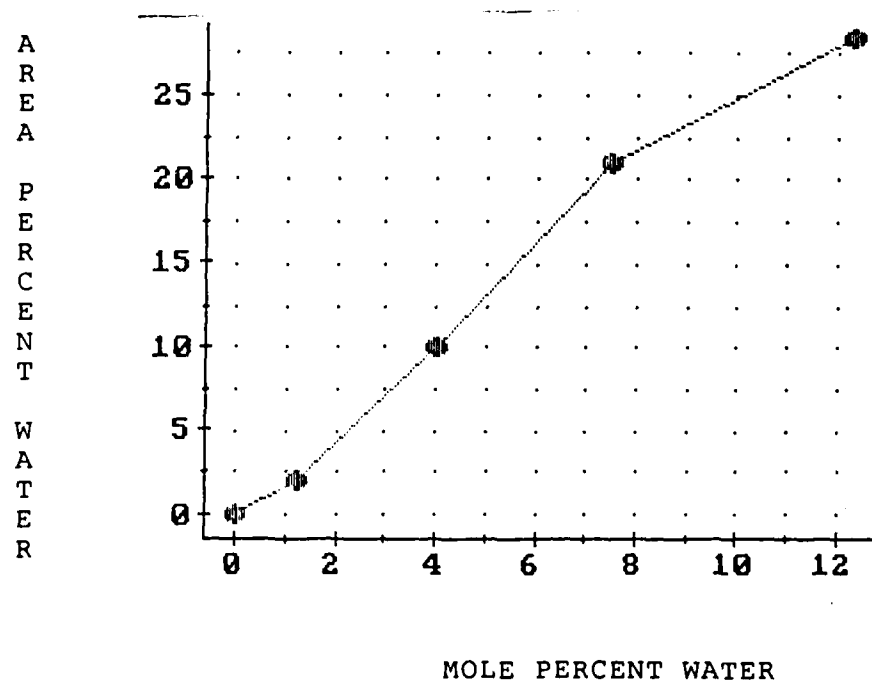process used by Crown Zellerbach to produce DMSO.[2]

APPENDIX I

MOLE PERCENT WATER

Figure A3: Calibration curve for gas chromatograph.

APPENDIX J

Energy Requirements

HEATING RATE ($^\circ$C/hr)	MIN. ENERGY REQUIRED (kcal)	THERMO. EFFICIENCY
2.0	0.83	0.18
3.0	1.02	0.16
4.5	0.93	0.17
5.3	0.67	0.11
5.4	C.o8	0.20
6.0	0.64	0.11
7.5	0.64	0.14
10.0	1.01	0.22
11.0	----	----
14.0	1.04	0.22
21.7	0.88	0.22
27.8	1.25	0.23

Table A1: The minimum energy requirements and the thermodynamic efficiencies for the different heating rates.

APPENDIX K

MOLE BALANCE

HEATING RATE	MOLES IN (gmmoles)					
(°C/hr)	FEED		SOLID		LIQUID	
	DMSO	WATER	DMSO	WATER	DMSO	WATER
2.0	21.9	2.42	4.05	0.03	17.85	2.39
3.0	21.9	2.40	5.59	0.06	16.31	2.34
4.5	21.9	2.42	5.05	0.04	16.85	2.38
5.3	22.0	2.32	3.79	0.01	18.21	2.31
5.4	21.6	2.72	4.48	0.05	17.12	2.67
6.0	21.9	2.42	3.50	0.01	18.40	2.41
7.5	22.2	2.12	3.79	0.02	18.41	2.10
10.0	21.9	2.42	5.45	0.07	16.45	2.35
14.0	22.0	2.32	5.87	0.08	16.13	2.24
21.7	21.6	2.72	4.48	0.06	17.12	2.66
27.8	21.5	2.82	6.15	0.10	15.35	2.72

Table A2: A mole balance for every heating rate except 11.0 °C/hr.

APPENDIX L

Sample Calculations

In this section, the sample calculations for determining the heating rate and a mole balance are given. Also, the energy requirements will be determined and this includes calculating the change in enthalpy for a separation and the change in entropy for a separation. Then the minimum energy requirements and the thermodynamic efficiency will be calculated.

(1) The heating rate for the trial performed on 19 FEB 86 will be calculated in this section. The heating rate was calculating by determining the time required to achieve a 3° C increase. In this manner, the computer would be allowed enough time to control any temperature oscillations. Sample 1 was taken at 16:45 and at a temperature of 4.125 ^{O}C. Sample 4 was taken at 17:08 and at a temperature of 7.125 ^{O}C.

$$\text{Heating Rate} = (\Delta T/\Delta t)(60 \text{ min}/1 \text{ hr}) \quad (L1)$$

$$= (3 \ ^O\text{C}/23 \text{ min})(60 \text{ min}/1 \text{ hr})$$

$$= 7.83 \ ^O\text{C/hr}$$

This calculation was performed for every 3° C increase and an arithmetic average was determined. The average was taken to be the heating rate for that trial.

(2) A mole balance for the trial with a heating rate of $\overline{3.0}$ ^{O}C/hr will determined in this section. The initial charge was 90.2 mole percent DMSO and had a mass of 1754 gm. The number of moles of DMSO was determined by calc lating an average molecular weight from the composition and then finding the total number of moles.

$$\text{Ave. MW} = MW_{DMSO} \times X_{DMSO} + MW_{water} \times X_{water} \quad (L2)$$

$$= 78.13 \text{ gm/gmmol} \times 0.902 + 18.02 \text{ gm/gmmol} \times 0.098$$

$$= 72.24 \text{ gm/gmmol}$$

$$N_{total} = \text{Mass of Charge / Ave. MW} \qquad (L3)$$

$$N_{total} = 1754 \text{ gm} / 72.24 \text{ gm/gmmol}$$

$$N_{total} = 24.3 \text{ gmmol}$$

$$N_{DMSO} = N_{total} \times X_{DMSO} \qquad (L4)$$

$$N_{DMSO} = 24.3 \text{ gmmol} \times 0.902$$

$$N_{DMSO} = 21.9 \text{ gmmol}$$

$$N_{water} = N_{total} - N_{DMSO} \qquad (L5)$$

$$N_{water} = 24.3 \text{ gmmol} - 21.9 \text{ gmmol}$$

$$N_{water} = 2.4 \text{ gmmol}$$

This method is also used to determine the number of moles of each component in the product. Therefore, the calculations will not be shown.

Ave. MW = 77.53 gm/gmmol

$$N_{total} = 5.65 \text{ gmmol}$$

$$N_{DMSO} = 5.59 \text{ gmmol}$$

$$N_{water} = 0.06 \text{ gmmol}$$

The number of moles in the liquid removed during the heating step can be determinedd by subtracting the number of moles in the product from the number of moles in the initial charge.

$$N_{DMSO} = 16.31 \text{ gmmol}$$

$$N_{water} = 2.34 \text{ gmmol}$$

(3) The energy requirements for the separation process with a 3.0°C/hr will be calculated in this section. To determine the energy requirements, the change in enthalpy and the change in entropy for the process must be calculated first.

$$W = \Delta H - T_i \Delta S \qquad (L6)$$

The change in entropy for this process for an ideal solution can be determined from Equation (L7).

$$\Delta S = \Delta S_{fract} - N_{DMSO} \times \Delta H_f / T_f \qquad (L7)$$

Therefore, the energy requirements can be calculated
from Equation (L8).

$$W = N_{DMSO} \times (1 - T_i/T_f) \times \Delta H_f - T_o \times \Delta S_{fract} \quad (L8)$$

where T_i is the operating temperature which is 285.4 $^\circ$K
and T_f is the freezing temperature which is 291.65 $^\circ$K.
The change in enthalpy for this process for an ideal
solution is the heat of fusion plus the difference in
heat capacities of the solid and the liquid over the
temperature difference of the process. The temperature
difference for this experiment was small, so this term
was considered negligible.

$$\Delta H = N_{DMSO} \times \Delta H_f \quad (L9)$$

$$\Delta H_f = 3227 \text{ cal/gmmol}$$

$$N_{DMSO} \times (1 - T_i/T_f) \times \Delta H_f = 5.59 \text{ gmmol} \times$$

$$(1 - 285.4/291.65)$$

$$3227 \text{ cal/gmmol}$$

$$= 386.6 \text{ cal}$$

The change in entropy for a fractionation step can be
calculated from Equation (L10).

$$\Delta S_{fract} = -R[B_1 \ln((B_1/B_0)/(A_1/A_0))$$

$$+ B_2 \ln((B_2/B_0)/(A_2/A_0))] \quad (L10)$$

where B is DMSO and A is water. The subscripts 0,1,and
2 are for the feed, the product, and the liquid removed
during the heating process, respectively.

$$B_0 = 21.9 \text{ gmmol} \quad A_0 = 2.40 \text{ gmmol}$$
$$B_1 = 5.59 \text{ gmmol} \quad A_1 = 0.04 \text{ gmmol}$$
$$B_2 = 16.31 \text{ gmmol} \quad A_2 = 2.36 \text{ gmmol}$$

$$\Delta S_{fract} = -1.99 \text{ cal/gmmol} \times {}^\circ K[5.59 \text{ gmmol} \times$$

$$\ln((5.59/21.9)/(0.04/2.40)) +$$

$$16.31 \text{ gmmol} \times$$

$$\ln((16.31/21.9)/(2.36/2.40))]$$

$$\Delta S_{fract} = -21.3 \text{ cal}/^\circ K$$

END
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